Explicit two cycle model in investigation of stochastic effects in diffusion regime of metastable phase decay

Victor Kurasov

February 2, 2008

Abstract

The theory for manifestation of stochastic appearance of embryos in the global decay of metastable phase has been constructed. The regime of droplets growth is supposed to be both free molecular one and diffusion one. The deviation for a mean droplets number from the value predicted by the theory based on averaged characteristics have been calculated. The value of dispersion for the distribution of the total droplets number in particular attempt has been also calculated analytically. Comparison with results of numerical simulation has been given and the correspondence between simulation and analytical approximate results is rather good.

The aim of this paper is to give analysis of decay in diffusion regime of the droplets growth in frames of the method given in [1] and corrected in [6]. This method is based on the following approximation

- Until the half of the nucleation period (in the time scale) the supersaturation remains unperturbed and the droplets appear independently.

- In the second half of the nucleation period the droplets appear under the supersaturation changed by the vapor consumption by the droplets appeared in the first part of the nucleation period.

The part of the droplets size spectrum which corresponds to the droplets appeared during the first part of the nucleation period will be called as the first part of spectrum, the remaining part will be the second part of spectrum.

Here this model will be generalized by means of the following changes:

1

- The duration of the first part of nucleation period will be not exactly the first half but it will be regulated by some parameter p instead of $1/2$.

- The regime of growth will be an arbitrary power law of growth (the power type is adopted only to present concrete formulas, it isn't principal here).

- It is supposed that the distribution of droplets in the first part of spectrum can differ from the distribution

$$P_0(N) \sim \exp(\frac{(N - \bar{N})^2}{2\bar{N}})$$

of N independently appeared droplets during the period of time corresponding to the mean value $\bar{N}$ of appeared droplets.

Now instead of the previous distribution the distribution with renormalized dispersion

$$P_r(N) \sim \exp(\frac{(N - \bar{N})^2}{2\psi\bar{N}})$$

will be used. Here ψ is parameter of renomalization. This change is initiated by the using of the property of self similarity of spectrums in the first iteration (see [5]) used for investigation of stochastic effects in [6].

The structure of consideration will be the following

- At first we shall present the formal generalized model

- Then the parameter p of the boundary between the first and the second parts will be calculated.

- In the last part the effect of the "growing volumes of interaction" will be described and it will be shown how to include this effect into already presented scheme.

- In Appendix the theory for the free molecular regime of growth will be presented. This theory was given in [6] but now some modifications and improvements have been made. So, a new variant can be found in appendix.

2

The main object of investigation will be the calculation of dispersion of the droplets distribution since the mean value will be very close to the characteristic calculated in frames of the theory based on the averaged characteristics (TAC), all arguments given for the free molecular regime of the droplets growth remain here practically the same [6], the only principally new feature is to use the theory with explicit profiles of density around the growing droplets [4].

The smallness of fluctuations which will be shown here plays a very important role in transition from the free molecular kinetics to the diffusion kinetics. Really, such transition was shown in [4] only in general features on the level of TAC and the possible giant fluctuations initiated by stochastic appearance of droplets would destroy this transition in frames of the known approaches. Fortunately the giant fluctuations don't appear and the justification of their absence lies in the moderate value of dispersion calculated here.

1 Calculation of dispersion

Here we shall analyze the situation with diffusion regime of metastable phase consumption. At it has been already noticed this situation is characterized by the growing volumes of interaction which produces additional difficulties. The growing volume of interaction means that the fixed point in the volume will be under influence of vapor consumers which appeared in a volume V with a center at this point and with a radius $\sqrt{4Dt}$ where t is a time counted from the consumer appearance up to a current moment and D is a diffusion coefficient. Certainly the last value can be regarded only as the rough estimate, the precise expression can be obtained only of the base of precise profiles of a substance gap [4].

At first we briefly follow the way to derive the estimate for dispersion proposed in [1] to use it for diffusion regime of metastable phase consumption. As we have noticed the formalism of a volume of interaction is a rather rough estimate (precise theory has to be based on a form of substance gap from [4]). Thus, the accuracy here is limited. So, in frames of adopted accuracy we shall use here only some rough way to estimate dispersion of a distribution and can use formalism from [1] with appropriate comments and modifications. This way is useful because it allows to understand formulas from [1] which were widely used in above consideration.

Here we suppose that the rate of embryos growth is given by

$$\frac{d\nu}{dt} \sim \nu^s$$

where ν is the number of molecules inside the embryo and s is a power parameter. We suppose that s takes values which are essentially greater than 0 (s isn't too small in comparison with 1) and essentially less than 1 ($1 - s$ isn't too small in comparison with 1). For the free molecular regime of metastable phase consumption $s = 2/3$, for the diffusion regime $s = 1/3$.

Then the characteristic ρ of a droplet defined as

$$\rho = \nu^{(1/s)+1}$$

grows with velocity independent on it's value

$$d\rho/dt \sim 1$$

The period of nucleation is divided in many elementary intervals with a length Δ (or Δ_i) in a ρ-scale, the average total number of interval in the whole nucleation period is M, the number of embryos N_i appeared during every elementary interval is supposed to be big $N_i \gg 1$.

The fact that the total number of intervals is M and their length is Δ (in estimates we can put it one and the same for all intervals, at least we can take the smallest length and attribute it to all intervals) means that

$$\Gamma \bar{f} (M\Delta)^{(\frac{1}{1-s}+1)} \sim (\frac{1}{1-s} + 1)\zeta(0) \ ,$$

where $\zeta(0)$ is the initial supersaturation, $\bar{f}$ is the initial average amplitude of embryos size spectrum [3], Γ is parameter from TAC [3]. Namely the last relation can be derived from the first iteration in TAC. It will be used to express $\bar{f}$ through M, Δ.

During every interval the increase $\delta\rho$ of the value ρ of already existing droplet will be

$$\delta\rho \sim \Delta\zeta(0)/\tau$$

with some characteristic time τ which will be dropped out in final formulas.

Denote by N_i the number of embryos appeared at i-th interval. The value $\bar{N}_i$ is the average N_i, $P_i(N_i)$ is the density distribution on N_i.

4

Denote by $N^{(i)}$ the number of embryos appeared at the first i-th intervals Δ. The value $\bar{N}^{(i)}$ is the average $N^{(i)}$, $P^{(i)}(N^{(i)})$ is the density distribution of $N^{(i)}$. It is important to stress that $\bar{N}^{(i)}$ isn't equal to $\tilde{N}^{(i)}$ which is the corresponding value completely calculated in frames of TAC (stochastically appeared droplets in the previous moments of time taken into account).

At the first P intervals (i.e. at the first part of nucleation period) the metastable substance consumption is negligible. Here $P = pM$ and p is parameter of constructions. Then for $k < P$ the distribution $P^{(k)}$ of the number of droplets $N^{(k)}$ appeared in the first k intervals is

$$P^{(k)}(N^{(k)}) \sim \exp\left(-\frac{(N^{(k)} - \bar{N}^{(k)})^2}{2\psi\bar{N}^{(k)}}\right)$$

and it is is a standard Gaussian distribution of k independent subsystems[1].

We introduce here the parameter of renormalization ψ to be able to fulfill calculations suggested in [6] based on the approximate similarity of nucleation conditions [5].

For $k > P$ the expression for $P^{(k)}$ will be formally the following

$$P^{(k)}(N^{(k)}) = \sum_{N_1,\ldots,N_P} \prod_{i=1}^{P} \hat{P}_i(N_i)\Omega$$

where

$$\hat{P}_i(N_i) \sim \exp\left(-\frac{(N_i - \bar{N}_i)^2}{2\psi N_i}\right)$$

$$\Omega = \sum_{N_{P+1},\ldots,N_{k-1}} \prod_{j=P+1}^{k-1} \hat{P}_j(N_j)\hat{P}_k\left(N^{(k)} - \sum_{l=1}^{k-1} N_l\right)$$

Here the function Ω is extracted because it corresponds to the second part of spectrum. The function Ω is superposition of independent subsystems and can be calculated explicitly

$$\Omega \sim \exp\left(-\frac{(N^{(k)} - \sum_{i=1}^{P} N_i - \sum_{j=P+1}^{k} \bar{N}_j)^2}{2\sum_{j=P+1}^{k} \bar{N}_j}\right)$$

The problem is that the values $\bar{N}_j$ standing in the last expression are unknown now. They are functions of all N_i, $i = 1,..,P$ (since the two

---

[1]Here and later without any notation we don't keep the preexponential factors before Gaussian distributions, they can be easily reconstructed by integration.

parts model is used). So, the distributions from the first group $i \leq P$ have the influence on Ω. This influence is given through the values $\bar{N}_j$. Now we shall get an expression for this value. At first we recall the exponential approximation which can be found elsewhere (see [3])

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{\Gamma}{\zeta_0} G_j)$$

Here G_j is the number of molecules in a liquid phase at j-th interval. For this value we can write

$$G_j = \sum_{i=1}^{j} N_i \rho_i^{(j)}{}^{\frac{1}{1-s}}$$

where $\rho_i^{(j)}$ is the "size" ρ of a droplet appeared at i-th interval at the moment corresponding to the j-th interval. Then

$$G_j = \sum_{i=1}^{j} N_i ((\Delta\zeta_0/\tau)j - (\Delta\zeta_0/\tau)i)^{\frac{1}{1-s}} = \sum_{i=1}^{j} N_i (j-i)^{\frac{1}{1-s}} (\Delta\zeta_0/\tau)^{\frac{1}{1-s}}$$

and

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{\Gamma}{\zeta_0} (\Delta\zeta_0/\tau)^{\frac{1}{1-s}} \sum_{i=1}^{j} N_i (j-i)^{\frac{1}{1-s}})$$

Now we have to get another expression for

$$K = \frac{\Gamma}{\zeta_0} (\Delta\zeta_0/\tau)^{\frac{1}{1-s}}$$

which appeared in the last relation. One has to clarify the meaning of M as the total number of intervals. Certainly, it is no more than a conditional definition to say that the end of nucleation is the moment when the averaged rate of nucleation falls e times in comparison with initial value. Then the corresponding equation will be

$$\frac{\Gamma}{\zeta_0} G_M = 1$$

We have to calculate G_M in some approximation. Let it be the ideal approximation, i.e. the first iteration [3]. Then

$$K \sum_{i=1}^{M} \bar{N}_1 (M-i)^{1/(1-s)} = 1$$

or

$$K\bar{N}_1 \sum_{i=1}^{M} (M-i)^{1/(1-s)} = 1$$

For $M \gg 1$ summation can be replaced by integration which gives

$$\sum_{i=1}^{M} (M-i)^{1/(1-s)} = \int_0^M (M-x)^{1/(1-s)} dx = \frac{M^{1/(1-s)+1}}{\frac{1}{1-s}+1}$$

and

$$K = (\bar{N}_1 \frac{M^{1/(1-s)+1}}{\frac{1}{1-s}+1})^{-1} \tag{1}$$

Then

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{\bar{N}_1 M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{j} N_i (\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}})$$

Here

$$\frac{1}{\bar{N}_1 M^{(\frac{1}{1-s}+1)}}$$

is simply the scaling factor. One can argue whether the style of calculation of G_M is appropriate. Really we used another approximation which differs from the two cycle model which we are going to use. But there is absolutely no sense how to calculate the last value. One can simply say that our model is to take the first part as $P = pM$ where the definition of M is given by (1). The problem is how to choose p.

We continue to simplify expression for $\bar{N}_j$, $j > P$. We recall that the droplets from the first part only consume vapor. Then we come to

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{\bar{N}_1 M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} N_i (\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}}) \tag{2}$$

Now we shall simplify the last formula. We make the following transformations:

- we add and subtract $\bar{N}_1$, which is the ideal mean value of droplets appeared during the elementary interval. Then

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} (1 + \frac{N_i - \bar{N}_1}{\bar{N}_1})(\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}})$$

7

and

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} (\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}} -$$

$$\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} \frac{N_i - \bar{N}_1}{\bar{N}_1}(\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}})$$

We can calculate $\sum_{i=1}^{P} (\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}}$. For $M \gg 1$

$$\sum_{i=1}^{P} (\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}} = (\frac{1}{1-s}+1) \int_0^P (j-x)^{\frac{1}{1-s}} dx$$

and since we suppose $1/3 < s < 2/3$ we have $1/(1-s) \gg 1$ and

$$\int_0^P (j-x)^{\frac{1}{1-s}} dx = \int_0^j (j-x)^{\frac{1}{1-s}} dx = (\frac{1}{1-s}+1)^{-1} j^{\frac{1}{1-s}+1}$$

for j which aren't too big in comparison with P (namely the parameter p will be chosen in such a way that P can not be too small in comparison with M and certainly j can not be essentially greater than M).

Then

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{M^{(\frac{1}{1-s}+1)}} j^{\frac{1}{1-s}+1} -$$

$$\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} \frac{N_i - \bar{N}_1}{\bar{N}_1}(\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}})$$

and

$$\bar{N}_j = \bar{N}_1 \exp(-\frac{1}{M^{(\frac{1}{1-s}+1)}} j^{\frac{1}{1-s}+1}) \exp(-\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} \frac{N_i - \bar{N}_1}{\bar{N}_1}(\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}})$$

Now we linearize the last exponent over

$$\frac{1}{M^{(\frac{1}{1-s}+1)}} \sum_{i=1}^{P} \frac{N_i - \bar{N}_1}{\bar{N}_1}(\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}}$$

This linearization is possible and it differs from linearization over

$$\frac{1}{M^{(\frac{1}{1-s}+1)}} \frac{N_i - \bar{N}_1}{\bar{N}_1}(\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}}$$

made in [1]. The linearization in [1] since we study fluctuations namely in N_i is very doubtful. In our approach we can see the compensation of fluctuation during the period comparable with the whole nucleation period and, thus, the linearization is possible.

It is necessary to stress that after the linearization one can not pretend on the derivation of deviation of the mean value of droplets from the value prescribed by TAC. Contrary to [1] we don't pretend on this but here we are interested only in dispersion. To prove the smallness of deviation of the mean value of total droplets from the value given by TAC one can use other approaches (see [6]).

Here we directly use $(\frac{1}{1-s}+1)(j-i)^{\frac{1}{1-s}}$ as the quantity of substance in droplets of a given size (the relative deviation of the size during the elementary interval is small) instead of inappropriate integration over constant distribution (it is stochastic and isn't constant) in [1].

In the zero approximation we get

$$\bar{N}_j = \bar{N}_1 \exp\left(-\frac{j^{(\frac{1}{1-s}+1)}}{M^{(\frac{1}{1-s}+1)}}\right)$$

In the first approximation

$$\bar{N}_j = \bar{N}_1 \exp\left(-\frac{j^{\frac{1}{1-s}+1}}{M^{\frac{1}{1-s}+1}}\right)\left(1 - \frac{1}{M^{\frac{1}{1-s}+1}}\sum_{i=1}^{P}\frac{N_i - \bar{N}_1}{\bar{N}_1}(1+\frac{1}{1-s})(j-i)^{\frac{1}{1-s}}\right)$$

Now we know the influence of embryos of big sizes and can directly analyze the numerator of Gaussian distribution for Ω. We have

$$\left(N^{(k)} - \sum_{i=1}^{P}N_i - \sum_{j=P+1}^{k}\bar{N}_j\right) = \left(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \sum_{i=1}^{P}\bar{N}_1 - \sum_{j=P+1}^{k}\bar{N}_j\right)$$

$$\left(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \sum_{i=1}^{P}\bar{N}_1 - \sum_{j=P+1}^{k}\bar{N}_j\right) =$$

$$\left(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) + P\bar{N}_1 - \sum_{j=P+1}^{k}\bar{N}_j\right)$$

Now we shall derive formula for $\sum_{j=P+1}^{k}\bar{N}_j$. We start with (2) where $\bar{N}_0 \equiv \bar{N}_1$ and get

$$\sum_{j=P+1}^{k}\bar{N}_j = \bar{N}_0 \sum_{j=P+1}^{k}\exp\left(-\frac{1}{M^{1/(1-s)+1}}\frac{1}{\bar{N}_0}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}N_i\right)$$

9

Since $M \gg 1$, $P \sim M$

$$\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}/M^{1/(1-s)+1} \approx j^{1/(1-s)+1}/M^{1/(1-s)+1}$$

So, one can come to

$$\sum_{j=P+1}^{k} \bar{N}_j = \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{M^{1/(1-s)+1}}) \exp(-\frac{1}{M^{1/(1-s)+1}}$$

$$\frac{1}{\bar{N}_0}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}N_i) \exp(\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}/M^{1/(1-s)+1})$$

Then

$$\sum_{j=P+1}^{k} \bar{N}_j = \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{M^{1/(1-s)+1}})$$

$$\exp(-\frac{1}{M^{1/(1-s)+1}}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i-\bar{N}_0)}{\bar{N}_0})$$

Now one can fulfill linearization of exponent over

$$\frac{1}{M^{1/(1-s)+1}}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i-\bar{N}_0)}{\bar{N}_0}$$

which leads to

$$\sum_{j=P+1}^{k} \bar{N}_j = \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{M^{1/(1-s)+1}})$$

$$(1-\frac{1}{M^{1/(1-s)+1}}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i-\bar{N}_0)}{\bar{N}_0})$$

The formula is ready.
Then

$$(N^{(k)}-\sum_{i=1}^{P}(N_i-\bar{N}_1)-P\bar{N}_1-\sum_{j=P+1}^{k}\bar{N}_j) = (N^{(k)}-\sum_{i=1}^{P}(N_i-\bar{N}_1)-P\bar{N}_1-$$

$$\bar{N}_0\sum_{j=P+1}^{k}\exp(-(j/M)^{1/(1-s)+1})(1-\frac{1}{M^{1/(1-s)+1}}\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i-\bar{N}_0)}{\bar{N}_0}))$$

The next transformation gives

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - P\bar{N}_1 - \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1})(1 - \frac{1}{M^{1/(1-s)+1}}$$

$$\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i - \bar{N}_0)}{\bar{N}_0})) =$$

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - P\bar{N}_1 - \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) +$$

$$\bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1})\frac{1}{M^{1/(1-s)+1}} \sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i - \bar{N}_0)}{\bar{N}_0})$$

Having noticed that

$$\tilde{N}^{(k)} = \bar{N}_1(P + \sum_{j=P+1}^{k} \exp(-\frac{j^{(\frac{1}{1-s}+1)}}{M^{(\frac{1}{1-s}+1)}})$$

is the mean number of droplets $N^{(k)}$ prescribed in the zero approximation by TAC, we come to

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - P\bar{N}_1 - \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) +$$

$$\bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1})\frac{1}{M^{1/(1-s)+1}} \sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i - \bar{N}_0)}{\bar{N}_0}) =$$

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \tilde{N}^{(k)} + \bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1})\frac{1}{M^{1/(1-s)+1}}$$

$$\sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i - \bar{N}_0)}{\bar{N}_0})$$

Now we shall change the order of summation and come to

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \tilde{N}^{(k)} +$$

$$\bar{N}_0 \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1})\frac{1}{M^{1/(1-s)+1}} \sum_{i=1}^{P}(\frac{1}{1-s}+1)(j-i)^{1/(1-s)}\frac{(N_i - \bar{N}_0)}{\bar{N}_0}) =$$

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \tilde{N}^{(k)} +$$

$$\sum_{i=1}^{P}(N_i - \bar{N}_0) \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)})$$

The last transformation leads to

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \tilde{N}^{(k)} +$$

$$\sum_{i=1}^{P}(N_i - \bar{N}_0) \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)}) =$$

$$(N^{(k)} - \tilde{N}^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_0)(1 -$$

$$\sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)}))$$

or

$$(N^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_1) - \tilde{N}^{(k)} +$$

$$\sum_{i=1}^{P}(N_i - \bar{N}_0) \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)}) =$$

$$(N^{(k)} - \tilde{N}^{(k)} - \sum_{i=1}^{P}(N_i - \bar{N}_0)a_i^{(k)})$$

where

$$a_i^{(k)} = (1 - \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)})$$

The last definition can be rewritten as

$$a_i^{(k)} = (1 - b_i^{(k)})$$

where

$$b_i^{(k)} = \sum_{j=P+1}^{k} \exp(-(j/M)^{1/(1-s)+1}) \frac{1}{M^{1/(1-s)+1}} (\frac{1}{1-s} + 1)(j-i)^{1/(1-s)}$$

Now we shall analyze denominator of Gaussian distribution for Ω. Here we can use $\bar{N}_j$ in the zero approximation and come to

$$\sum_{j=P+1}^{k} \bar{N}_j = \tilde{N}^{(k)} - P\bar{N}_1$$

The use of zero approximation is based on the following simple estimate. Really, the last linearization is based on the smallness mainly of the parameter which can be simply neglected in denominator since

$$\sum_{j=P+1}^{k} \exp(-(\frac{j}{M})^{1/(1-s)+1})$$

isn't too small.

Now we can directly go to the calculation of $P^{(k)}(N^{(k)})$ for $k > P$. The starting formula is

$$P^{(k)}(N^{(k)}) = \int_{-\infty}^{\infty} d(N_1 - \bar{N}_1)... \int_{-\infty}^{\infty} d(N_P - \bar{N}_P) \prod_{i=1}^{P} \exp(-\frac{(N_i - \bar{N}_1)^2}{2\psi\bar{N}_1})$$

$$\exp(-\frac{[N^{(k)} - \tilde{N}^{(k)} - \sum_{i=1}^{P} a_i^{(k)}(N_i - \bar{N}_1)]^2}{2(\tilde{N}^{(k)} - P\bar{N}_1)})$$

(3)

where we because of $\bar{N}_i \gg 1$ have replaced summation by integration. The limits of integration can be infinite ones because of $\bar{N}_i \gg 1$ and estimates predicted by Gaussian distribution.

To fulfill integration we have to use a simple formula

$$\int_{-\infty}^{\infty} \exp(-\frac{x^2}{c}) \exp(-\frac{(lx+d)^2}{b}) dx \sim \exp(-\frac{d^2}{b+l^2 c})$$

We have to use this formula P times with

$$x \sim x_i = N_i - \bar{N}_1$$

$$c \sim c_i = 2\psi\bar{N}_1$$

$$l \sim l_i = -a_i^{(k)}$$

$$b \sim b_i = 2(\tilde{N}^{(k)} - P\bar{N}_1)$$

13

This leads to

$$P^{(k)}(N^{(k)}) \sim \exp(-\frac{(N^{(k)} - \tilde{N}^{(k)})^2}{2D^{(k)}})$$

where dispersion $D^{(k)}$ is given by

$$D^{(k)} = \tilde{N}^{(k)} - (P - \psi \sum_{i=1}^{P} a_i^{(k)^2})\bar{N}_1$$

Now we can calculate dispersion at infinite k. Since $M \gg 1$ we can substitute summation by integration. The number of interval corresponds to the variable $z * M$, then $z = 1$ corresponds to the end of nucleation.

Since

$$\tilde{N}^{(\infty)} = \bar{N}_1(P + \sum_{j=P+1}^{\infty} \exp(-(\frac{j}{M})^{1/(1-s)+1})) \approx M\bar{N}_1\alpha$$

$$\alpha \equiv \int_0^{\infty} \exp(-x^{1/(1-s)+1})dx$$

then

$$D^{(\infty)} = \tilde{N}^{(\infty)}(1 - (1 - \psi)\frac{P}{M\alpha} - \frac{2\psi}{\alpha}\frac{1}{M}\sum_{i=1}^{P} b_i^{(\infty)} + \frac{\psi}{\alpha}\frac{1}{M}\sum_{i=1}^{P} b_i^{(\infty)^2})$$

One can easily calculate $b_i^{(\infty)}$:

$$b_i^{(\infty)} = \frac{1/(1-s)+1}{M^{1/(1-s)+1}}\sum_{j=P}^{\infty} \exp(-(\frac{j}{M})^{1/(1-s)+1})(j - i)^{1/(1-s)}$$

$$\rightarrow (1/(1-s)+1)\int_p^{\infty} \exp(-x^{1/(1-s)+1})(x - y)^{1/(1-s)}dx$$

Also one can note that

$$\frac{1}{M}\sum_{i=1}^{P} \rightarrow \int_0^{p} dy$$

Then

$$D^{(\infty)} = \tilde{N}^{(\infty)}(1 - (1 - \psi)\frac{p}{\alpha} - \frac{\Psi}{\alpha}\beta)$$

where

$$\beta = \beta_1 - \beta_2$$

14

$$\beta_1 = 2(1/(1-s)+1) \int_0^p dy \int_p^\infty dx \exp(-x^{1/(1-s)+1})(x-y)^{1/(1-s)}$$

$$\beta_2 = (1/(1-s)+1)^2 \int_0^p dy (\int_p^\infty dx \exp(-x^{1/(1-s)+1})(x-y)^{1/(1-s)})^2$$

This result can be directly calculated.

2 Calculations of parameters of the model

To compare analytical constructions with the real value of dispersion we shall present numerical simulations.

The results for the mean value of droplets calculated in units of the droplets number calculated in TAC as function of the droplets number calculated in TAC are presented in figure 1.
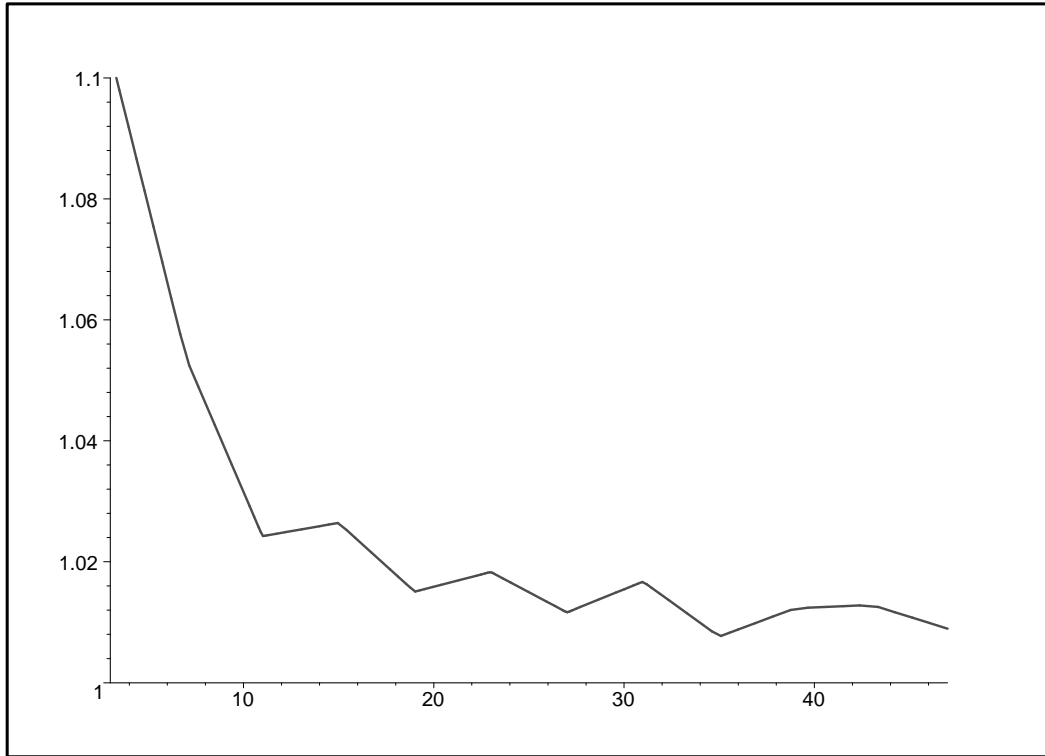

Figure 1: Mean value of the droplets number

The relative dispersion as a function of the mean number of droplets is shown in figure 2.
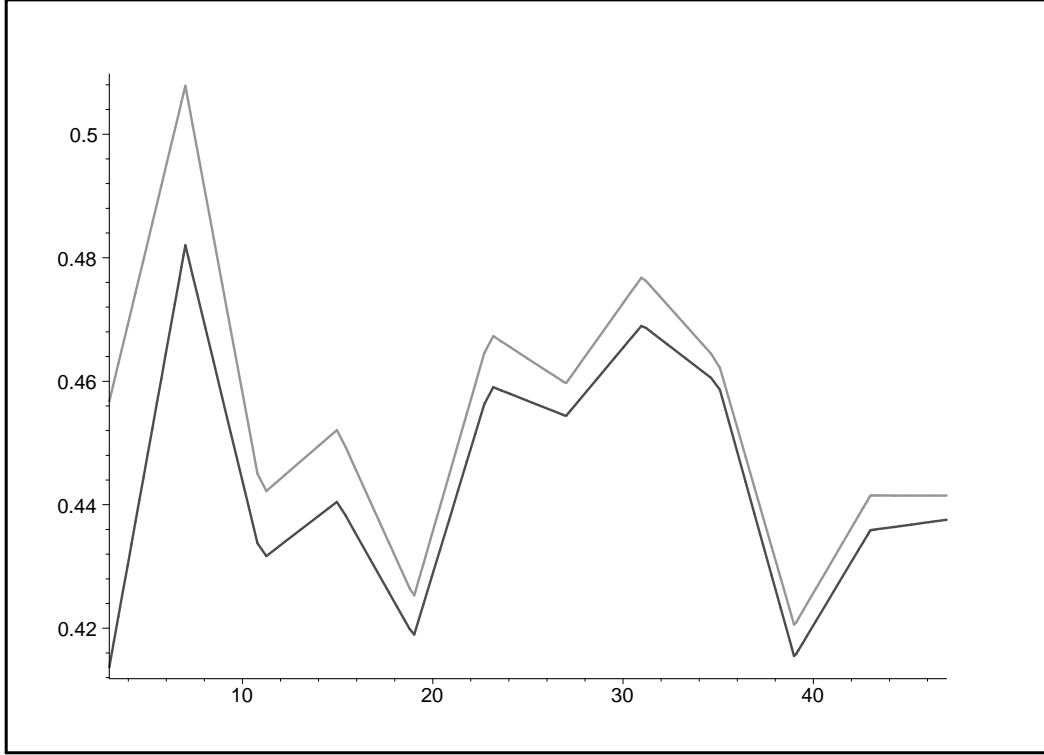
Figure 2: Dispersion

Now we shall perform calculations. We study equation

$$g(x) = \frac{5}{2} \int_0^z \exp(-g(x))(z - x)^{3/2} dx$$

Namely the coefficient $\frac{5}{2}$ corresponds to the final formulas in the previous section.

At first we calculate the form of spectrum. It is shown in figure 3. Two curves are drawn. The upper one in the second iteration approximation, the lower curve is the first iteration approximation. The spectrum lies between these curves.

One can see that the characteristic length of spectrum is $x_0 \approx 1.2 \div 1.25$.

The total number of droplets is $N_{TAC} = 0.9292$. The first iteration gives $N_{first} = 0.8773$.

Now we investigate the two cycle model. The relative number of droplets as a function of the boundary p is shown in figure 4.
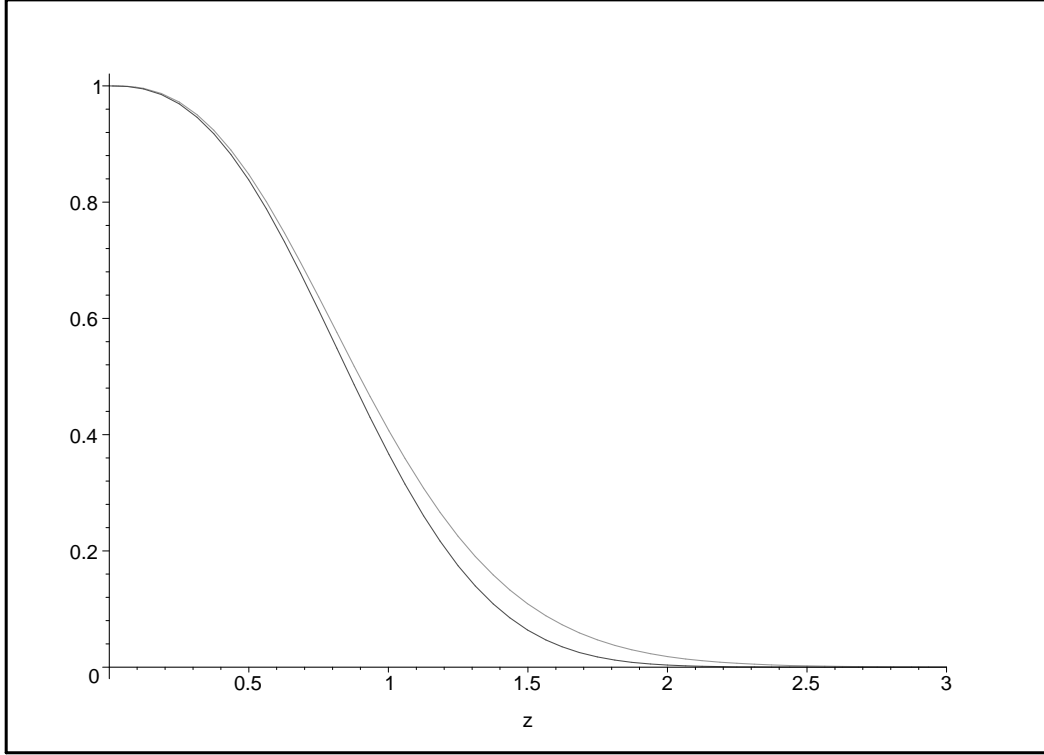
Figure 3: The form of spectrum in TAC

Here two curves are drawn. The upper corresponds to the number of droplets referred to the number of droplets in the first iteration, the lower curve is referred to the precise value of the droplets number. One can see that the deviation of the second curve is two times closer than the deviation of the first curve in the value of minimum. The minimum is attained at $p_0 = 0.64$ which is approximately the 55 percent of x_0 (the same part as in the free molecular regime! [6]).

Now we calculate β. The values β_1 and β_2 are drawn in figure 5. One can see that the behavior of β is mainly governed by behavior of β_1.

The ratio β_2/β_1 is drawn in figure 6.

One can see that there is no extremum of the ratio. So, there is no special boundary which provides the quickest convergence of the chain β_1, β_2, ... and one has to use $p_0 = 0.64$ going from the most precise approximation for number of droplets as a criterium for such boundary. Also one can see that the ratio is small for all p.
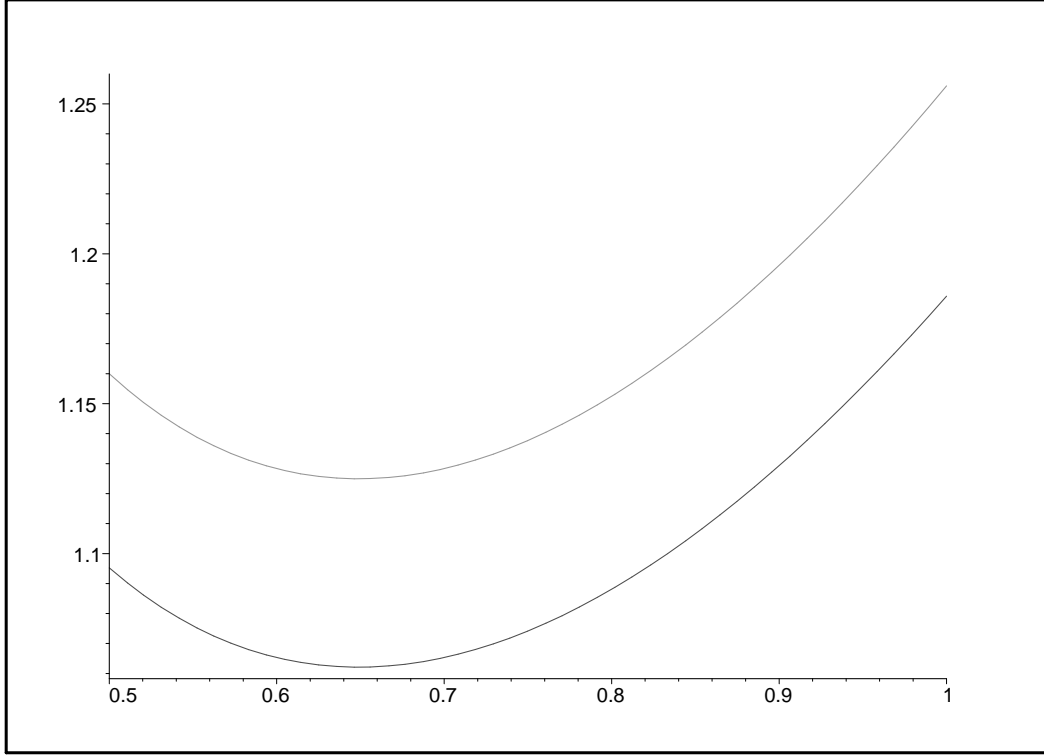
17

Figure 4: Mean value of the relative droplets number in two cycle model

The value of relative dispersion calculated according to

$$D = 1 - \beta/\alpha$$

is drawn in figure 7.

There are two curves: the upper is dispersion calculated with precise number of droplets, the lower is dispersion calculated with the number of droplets calculated in the first iteration. Both curves have extremum at $p = 0.68$. Even for the lowest curve all values are greater than 0.54 while the real value is 0.44.

If we take into account that α also has to be calculated in two cycle model. Then the value of relative dispersion[2] as a function of the boundary p ini the two cycle model is drawn in figure 8.

One can see that practically nothing has been changed. Minimum is at 0.67, the value of minimum is near 0.6.

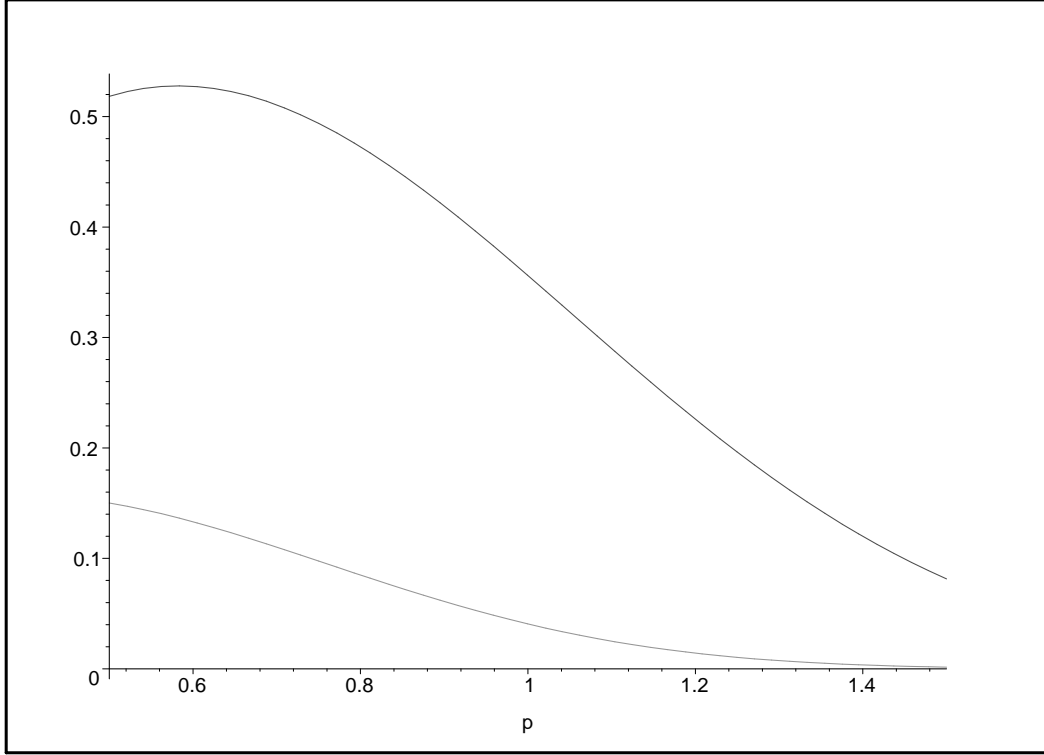[2]More precisely there is a square of relative dispersion.

Figure 5: Values β_1 and β_2.

Now we try approach based on similarity of nucleation conditions [5]. We start with the infinite upper boundary in formulas for β_1 and β_2.

At first we shall show the result for renormalization of dispersion when for α we take the result from the two cycle model. The result is shown in figure 9.

At $p = 0.64$ the value of ψ will be 0.46, at $p = 0.68$ the value of ψ will be 0.43.

When we put $\alpha = 0.92$ which is the result in the precise solutuion we came to the result shown in figure 10. Practically nothing has been changed.

Now we shall restrict the upper limit of integration by $z = 1$ (this is the current moment of observation). At first we draw the number of droplets as function of p in figure 11.

We see that the number of droplets has minimum at $p = 0.43$. This value has to be chosen as p in calculation of dispersion.

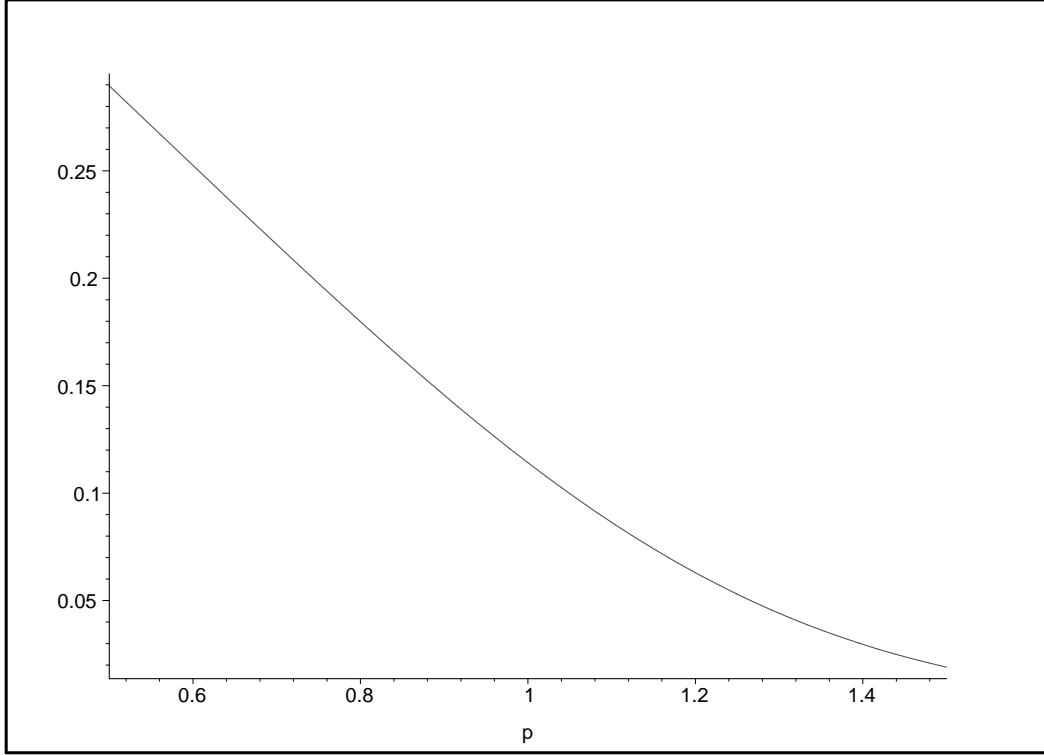Then the value of relative square of dispersion can be calculated and it

Figure 6: Ratio β_1/β_2

is drawn in figure 12.

We see that at $p = 0.43$ the value of dispersion is near 0.64 and it is far from the expected value. It resembles the calculation without similarity taken into account.

It is interesting to note that in diffusion regime the values of relative dispersion ψ calculated in the model with the upper boundary ∞ and with the upper boundary 1 are practically the same. This is true for moderate p (more concrete $p \leq 0.7$).

An explanation of this property is the following: under the free molecular regime of droplets growth the droplets appeared in the first moments of time grow so rapidly that it was very important to know until what sizes (or until what moment) they will grow. So, the duration of the nucleation period was very important. Under the diffusion regime of growth this effect is much more weak. So, the position of the boundary isn't so essential.

For $p \leq 0.5$ the value $1 - \beta/\alpha$ is also close to these values.
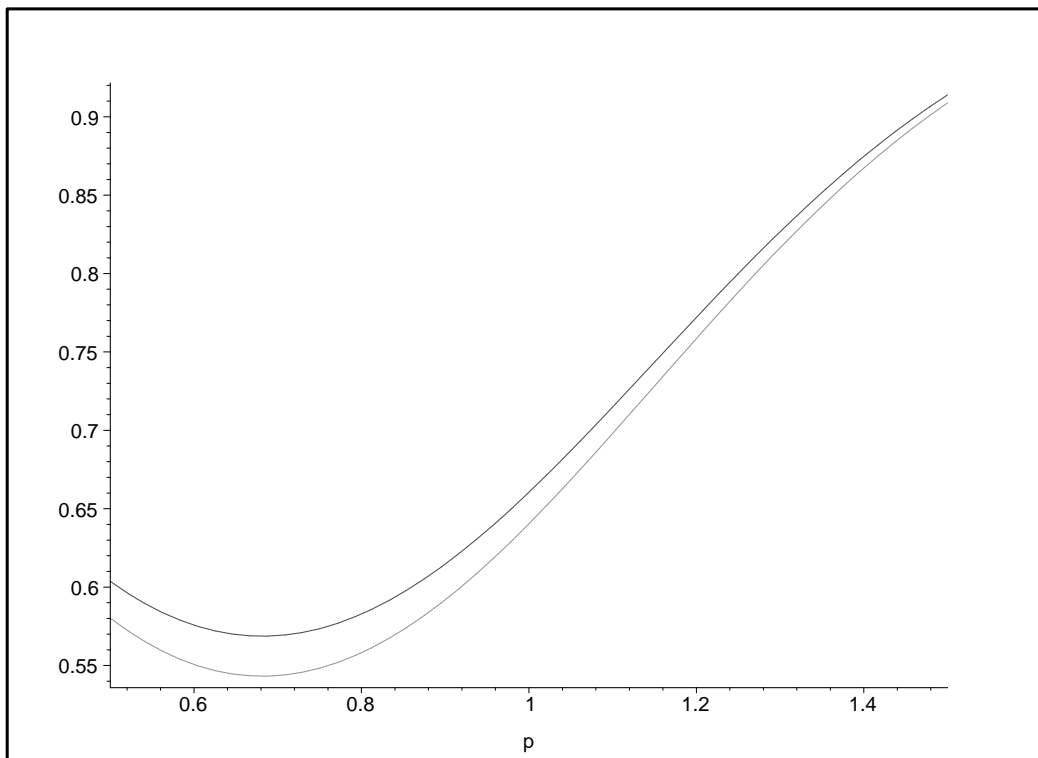
Figure 7: The relative square of dispersion in the two cycle model.

The explanation lies also in collective character of stochastic effects initiated under the diffusion regime of droplets growth.

The question to decide is whether we have to take p from extremum for α calculated with the upper boundary ∞ or with the upper boundary 1. From the first view it seems that the boundary 1 is preferable because β_1 and β_2 are calculated with the upper boundary 1. But the extremum for α corresponds to the value $\alpha = 0.815$. This value is smaller than α calculated in the first iteration, i.e. $\alpha_1 = 0.8773$ and smaller than this value calculated in the precise solution $\alpha_{pr} = 0.9292$. So, at extremum (it is a minimum) of the model with the upper boundary 1 the deviation from the precise value attains maximum. At the upper boundary ∞ the value of α is always bigger than 1 which is greater than α_1 and α_{pr}. So, here the extremum is really the closest value to precise solution. Then it has a real physical meaning. So, it is reasonable to take p corresponding to the extremum of α with the upper boundary ∞.
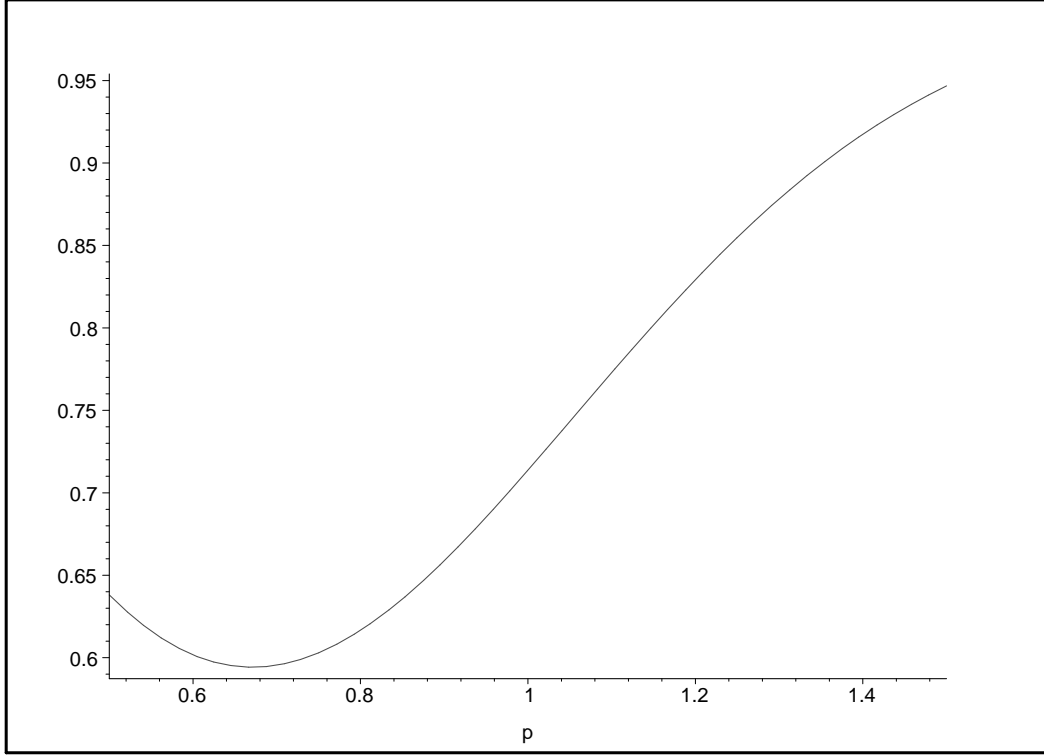
Figure 8: The relative square of dispersion in the two cycle model. Account of the change of the droplets number.

Calculations give $p = 0.65$ and $\psi = 0.49$. This value is calculated on the base of β_1 and β_2 with the upper boundary 1. The value $\psi = 0.49$ is rather close to result of numerical simulation $\psi = 0.44$. Certainly, the relative error is one tenth and the methods based on the explicit two cycle models cannot give more precise results.

One can note the following curious result. Evidently, when we calculate ψ for $p = 0.65$ with the upper boundary 1 we come to $\psi = 0.46$ which is practically the necessary result. But this coincidence is no more than an occasional one. When we try the same procedure for the free molecular regime we come to $\psi = 0.55$ (here $\psi = 0.55$) which is far from numerical result $\psi = 0.64$.

Having estimated the value of deviation of $\psi = 0.49$ from $\psi = 0.44$ one has to note that it is much smaller than the deviation of $\psi = 0.59$ of the value $1 - \beta/\alpha$ in its minimum from $\psi = 0.44$. So, the modification made
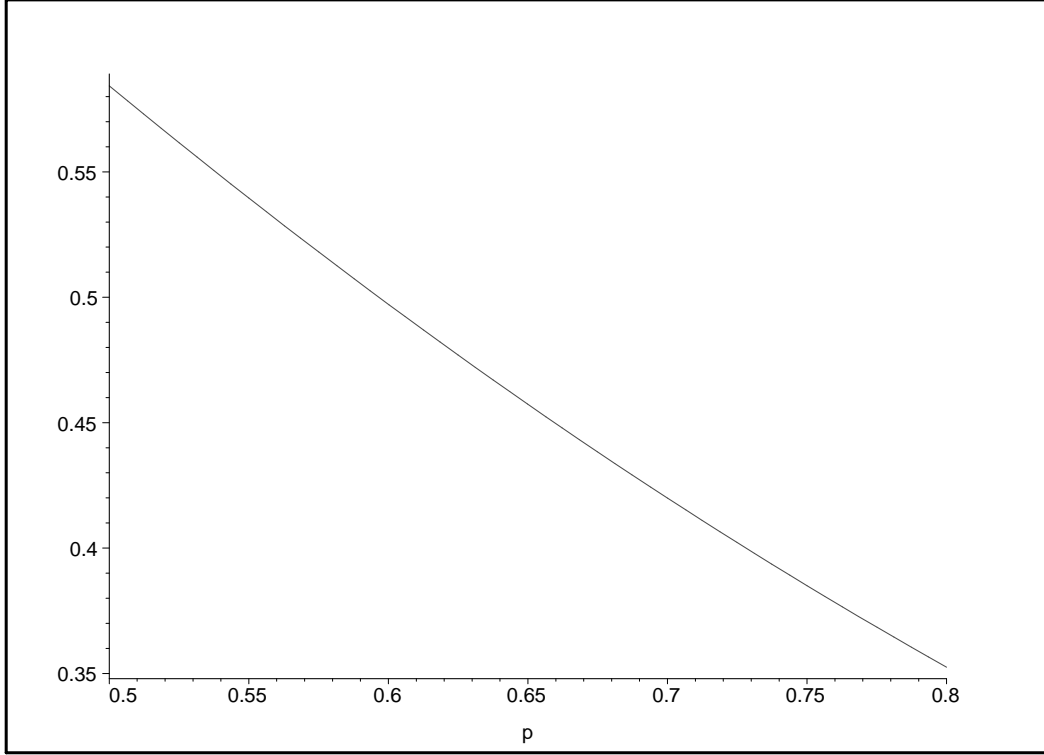
Figure 9: The relative square of dispersion in the similarity model. Account of the change of the droplets number in two period model.

here really have a real sense.

3 The effect of growing volumes of interaction

What shall we do to take into account the growth of the volume interaction in diffusion regime of growth? It is necessary to rewrite formula (3). We can substitute in $\exp(-\frac{(N_i - \bar{N}_1)^2}{2\bar{N}_1})$ the denominator $2\bar{N}_1$ by another denominator which corresponds to the growing volume of interaction. Then $\bar{N}_1$ has to be substituted by $\bar{N}_1 const(j - i)^{5/2}$ with some known *const*. It means that the characteristic half-width $\sqrt{\bar{N}_1}$ has to be substituted by $\sqrt{\bar{N}_1 const(j - i)^{5/2}}$. One can not apply directly this substitution in $\exp(-\frac{(N_i - \bar{N}_1)^2}{2\bar{N}_1})$ but only ap-
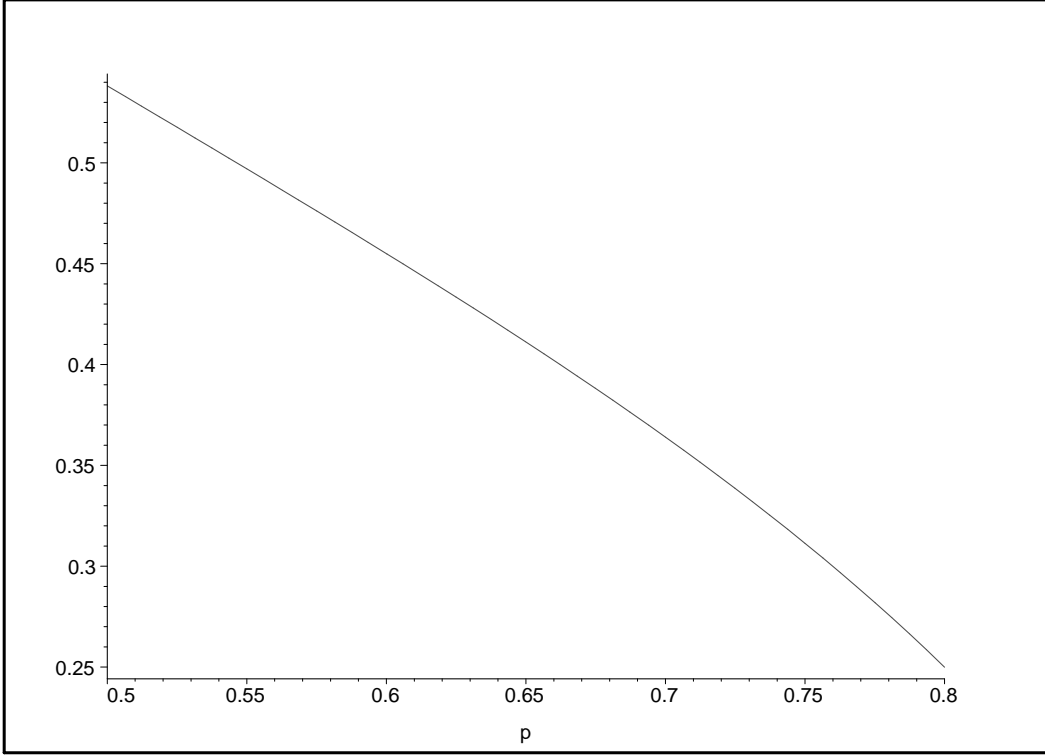
Figure 10: The relative square of dispersion in the similarity model. The droplets number is taken from precise solution.

proximately in expression for $a_i^{(k)}$ which now will be

$$a_i^{(k)} = 1 - \frac{5/2}{M^{5/2}} \sum_{j=P+1}^{k} \exp(-\frac{j^{5/2}}{M^{5/2}})(j-i)^{(\frac{1}{1-s}+1)-5/2}/const$$

with some known *const* and an appropriate renormalization.

In diffusion regime

$$\frac{1}{1-s} + 1 - \frac{5}{2} = 0$$

and there is absolutely no effect. It means that kinetics of nucleation will be absolutely different. It is described in [4]. The most strong effect will take place in the free molecular regime where $\frac{1}{1-s} + 1 - 5/2 = 3/2$

Now we shall estimate the effect of the dispersion variation. We see

$$D^{(\infty)} \sim \tilde{N}^{(\infty)}(1 - \frac{1}{\alpha}(2(\frac{1}{1-s}+1) \int_0^p dx \int_p^\infty dz(z-x)^{\frac{1}{1-s}+1-5/2}\exp(-z^{5/2})$$
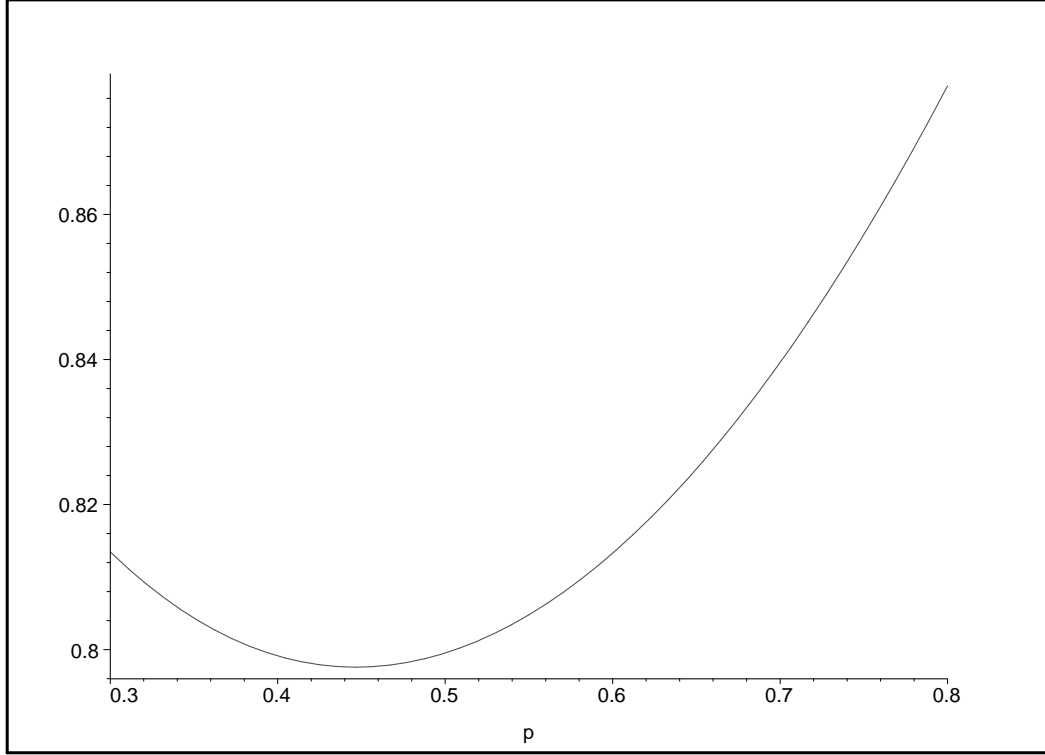
24

Figure 11: The number of droplets until the current moment.

$$-(\frac{1}{1-s}+1)^2 \int_0^p dx(\int_p^\infty dz(z-x)^{\frac{1}{1-s}+1-5/2} \exp(-z^{5/2}))^2))$$

Note that the last relation has to applied to the subsystem with the size $\sqrt{4Dt_n}$ where t_n is the duration of the nucleation period. Then we have to take the superposition of these independent subsystems.

We see that in the majority situations we can approximately neglect $(j-i)^{\frac{1}{1-s}+1-5/2} \approx (j-i)^0 = 1$ and see that then

$$D^{(\infty)} \approx \tilde{N}^{(\infty)}$$

and there is no effect.

Nevertheless the deviation in the number of droplets from the value calculated on a base of averaged characteristics exists. We have to divide the whole system into subsystems of the size $\sqrt{4Dt_n}$, then determine the number of droplets in this subsystem $\tilde{N}_{tot}^{subs}$ obtained on the averaged characteristics,

25

Figure 12: Relative square of dispersion up to the current moment. Account of the change of the droplets number.

then determine the deviation δN_{tot}^{subs} from the values calculated in TAC and then the whole deviation in the whole number of droplets N_{tot} from the value based on the averaged value $\tilde{N}_{tot}$ will be

$$\delta N_{tot} = \delta N_{tot}^{subs} \frac{\tilde{N}_{tot}}{\tilde{N}_{tot}^{subs}}$$

These procedures completely solve the problem.

One has also to note that the use of monodisperce approximation [2] leads to the absence of the problem of growing volume because the characteristics governing the nucleation period have been determined only in one moment of time. The problem here is a justification of monodisperse approximation to the calculation of fluctuation effects.

26

4   Appendix

Here we shall present the two cycle model with a fixed boundary in kinetics of the metastable phase decay under the free molecular regime of the droplets growth. This question was completely investigated in [6] but during the last two years our view on this problem was slightly modified and the modern state is described below.

Systematic investigations of the first order phase transitions are performed since Wilson [7]. The classical theory of nucleation [8] gave expressions for all main characteristics of stationary process of nucleation. This allowed to investigate a global picture of the phase transition. A set of papers [9] was devoted to model pictures of the global kinetics of nucleation. Here we shall also consider the global picture of the phase transition. One can note that all cited publications [9] were based on averaged nucleation rates. Here we shall consider stochastic appearance of embryos and outline the stochastic manner of appearance.

Recall briefly the main features of phase transition. Suppose that in initial moment of time there exists a metastable state. Then the embryos of a new phase begin to appear in the metastable system. The average rate of appearance is given by [8]. Then the embryos begin to grow and to consume the vapor, metastability falls and the rate of nucleation, i.e. the rate of appearance of new embryos falls also. The vapor consumption occurs in a time scale in a very sharp avalanche manner.

It is clear that during the nucleation period the new supercritical formations of the new phase appear with some fixed probability, but they appear in stochastic manner. So, the stochastic appearance of relatively big number of droplets leads to very rapid stochastic consumption of vapor. Stochastic appearance of relatively small number of droplets leads to delay of the vapor exhaustion and to excess of droplets appearance in next moments of time. But it seems that this excess can not compensate the opposite effect of the absence of embryos in first moments of time. It seems that the total number of droplets will differ from the average value. This is the naive reason why stochastic effects of nucleation have to be taken into account.

In a system with macroscopic sizes due to a giant value of the Avogadro number there appears some rather big number of droplets. It allows to use the averaged characteristics to construct kinetics of a nucleation process. Precise kinetic approach based on averaged characteristics is described in [3]. In [3] the time evolution is completely constructed.

After the formulation of integral equations (see [3]) one can introduce "elementary intervals of nucleation" - the intervals where the state of the system changes negligibly small. In macroscopic systems the total number of droplets is so big that at every elementary interval there appears a great number of droplets ΔN. On the base of traditional thermodynamics one can state that the relative fluctuation $\delta \Delta N / \Delta N$ of droplets formed at elementary interval is small and has an order of $(\Delta N)^{-1/2}$. This remark completely solves a problem of justification of nucleation description based on averaged characteristics.

Since it is possible to extract elementary intervals where thermodynamic parameters and the nucleation rate have small variations there is no need to take care about the stochastic corrections.

In experimental investigations one can not study quite macroscopic systems because the most popular data is the number of droplets and to fulfill the calculation of this number one can not have too many droplets[3]. After the theory based on the averaged characteristics has been presented it became possible to investigate the stochastic effects in kinetics of nucleation, i.e. the effects of stochastic appearance of droplets. Recently there appears a set of papers [10], [1], [11] where a stochastic effects (the effects of fluctuations of droplets formation) were described and investigated. One can extract two approaches which were formulated in [10] and in [1]. Although [1], [11] were written by the same authors of [10] these authors didn't hesitate that the theories formulated in [1] , [10] gave different results. So, at least one has to analyze approaches [10], [1] and decide whether there is a true result among these approaches and how it can be used to construct the adequate description of the nucleation process.

One has to specify a formulation of the problem of our investigation.

In [1], [10] it was proposed to establish corrections to the total number of droplets N appeared in the system. It was supposed that these corrections are functions of N. To demonstrate the error of this approach it is sufficient on one hand to take two identical systems then to calculate them separately and to add results or on the other hand to calculate correction directly for the total system. The results will be different.

One has to determine a real volume to which one has to refer the number of droplets. It is simple to do with the help of results from [4]. In that

---

[3]One can not simply calculate the infinite number of droplets. The upper limit of the number of droplets which can be noticed on a photo image is about several dozens.

28

paper the kinetics of nucleation for diffusion regime of droplets growth was constructed. It was shown that a solitary droplet perturbs vapor up to distances of an order $\sqrt{4Dt}$, where D is a diffusion coefficient, t is a time from a moment of droplet formation up to a current moment. As an estimate one can take as t a time t_1 of the whole nucleation period duration[4].

The last remark allows to give a new definition of the volume V_{el} where the number N_{el} of interacting (mainly through the vapor exhaustion) droplets is formed. Namely this value has to be regarded as a volume of a system in approach [10], [1]. This volume is

$$V_{el} = 4\pi(4Dt_1)^{3/2}/3$$

If the sizes of the system are smaller than this value one has to take the volume of the system as this value. But such a small system can be hardly regarded as a macroscopic one. At least one has to analyze carefully the boundary conditions for the system.

Naturally, the droplets appeared at different moments of time perturb initial phase up to different distances. So, one can regard above formulas only as estimates. Some more rigorous equations can be found in [13].

The number of droplets N_{el} isn't too big as N is. So, an analysis of stochastic effects has a real sense. It is interesting now to get all correction terms which are ascending with the number of droplets (but not only a leading term). To solve this task one has to modify approaches from [1], [10].

Complexity of this problem appears here because one can not directly use equations based on the theory with averaged characteristics. In [1], [10] some properties of solution of the theory on the base of averaged characteristics (TAC) were the starting points for constructions. This supposition was adopted without any justification. So, at first we have to decide whether it is possible to start with TAC.

We shall consider the situation of decay of metastable phase. The new dimensionless parameter - the number of droplets destroys the universality observed in [3] for the theory based on averaged characteristics. Moreover, it is difficult even to formulate the system of equations. This radically complicates the problem.

The possibility to use the effective monodisperse approximation formulated in [2] was used in [10] without any justifications. Generally speaking this property can not be directly used to calculate stochastic corrections.

---

[4]The nucleation period is a period of intensive formation of droplets.

One has to analyze whether this conclusion leads to an error made in [10]. Here we have to formulate more correct constructions.

Both approaches from [1] and from [10] declared that they used the following property observed in [3] in frames of TAC:

"The droplets formed at the beginning (i.e. at the first half) of the nucleation period are the main consumers of vapor".

This property is valid [3], but it is substituted in reality in [10], [1] by the following statement:

The main source of stochastic effects are the free fluctuations of droplets formed at the beginning (i.e. at the first half) of the nucleation period. They govern the fluctuations of all other droplets.

The last statement seriously differs from the first one. To get credible results it was necessary to balance the fluctuation effects from the first half of spectrum by the corresponding reaction of remaining part of spectrum. Then, at least this approach needs some special justifications. So, one has to use some new constructions which are presented below.

The application of the model approximation which was in reality done in [1], [11] will lead to some errors. But due to universality of solution [3] the errors can not be be too big. Qualitatively everything is suitable, but precision will be not so high.

The same conclusion will be valid for any approach based on some model behavior of supersaturation (justification is valid for a vapor consumption in TAC, but not for stochastic effects). Namely, in [1] was used an artificial approximation where at the first half of the nucleation period the conditions of nucleation are the ideal ones and at the second half the conditions of nucleation are governed by the droplets formed at the first half. Here in current paper the final result will be more precise and it will be not based on rather spontaneous artificial choice of some parameter as it was done in [1] where this parameter was put to to $1/2$. In [1] it is supposed that until some moment (it is chosen in [1] as a half of nucleation period) the droplets are formed under ideal conditions and namely these droplets determine a vapor consumption. In reality this approach taken from [12] (page 310) was used in [1] in slightly another sense. It is supposed that droplets formed during a first half of nucleation period are the main source of stochastic effects. The last statement was not justified in [1] and it is rather approximate. The relative correctness of a result was attained due to specific compensation of different errors of approximations used in [1]. It is necessary to stress that the the mentioned model was used in [12] to justify a strong inequality and

the high precision of constructions was not essential. But in [1] this model was the source of numerical result.

All arguments listed above lead to necessity of reconsideration which will be made in this publication. A plan of narration will be the following one

- Having considered the interaction of stochastic deviations of the number of droplets appeared during the elementary intervals of nucleation we shall see that stochastic effects are at least moderate.

- A moderate scale of stochastic effects allows to seek the solution on the base of the theory with averaged characteristics. But we have to take stochastic effects from all droplets formed during the nucleation period.

- The possibility to take into account the influence of stochastic deviations of all droplets can be provided by the property of the self similarity of nucleation conditions during the nucleation period. This property can be considered in two senses - 1) in the local differential sense and 2) in the integral sense in frames of the first iteration in the iteration procedure in TAC [15]. The local property will be used in justification of the smallness of stochastic effects and the integral property will be used to calculate the stochastic corrections of the whole nucleation period.

All analytical results will be checked by computer simulation and a coincidence will be shown.

All mentioned constructions will be valid for an arbitrary first order phase transition. The law of droplets growth here will be a free molecular one, then the linear size of droplet grows with velocity independent from its value. Consideration of other regimes can be formally attained in frames of the current approach by some trivial substitutions, but one has to take into account that the new regime requires new approaches to construct nucleation kinetics as it is shown in [4]. So, one can not agree with [10] where it is stated that one of results is an account of stochastic effects in a diffusion regime of droplets growth. This effect has to be taken into account principally in another manner by application of methods presented in [14].

31

4.1 Some characteristic features of decay kinetics

We begin with the theory based on averaged characteristics. It is supposed to be known [3], that the supersaturation ζ behavior can be determined after certain renormalizations by the following equation

$$\psi(z) = \int_0^z dx (z-x)^3 \exp(-\psi)$$

on function ψ which is the relative renormalized deviation of supersaturation from the initial value. Variables x and z can be considered as equivalent ones. A good approximation for solution and for a distribution of the droplets number over time (or over liner sizes of droplets) which is proportional to $\exp(\psi)$ is

$$f_1 = \exp(-z^4/4). \tag{4}$$

The form of f_1 is given by fig.13. It is seen that approximately at $z_0 = 1.25$
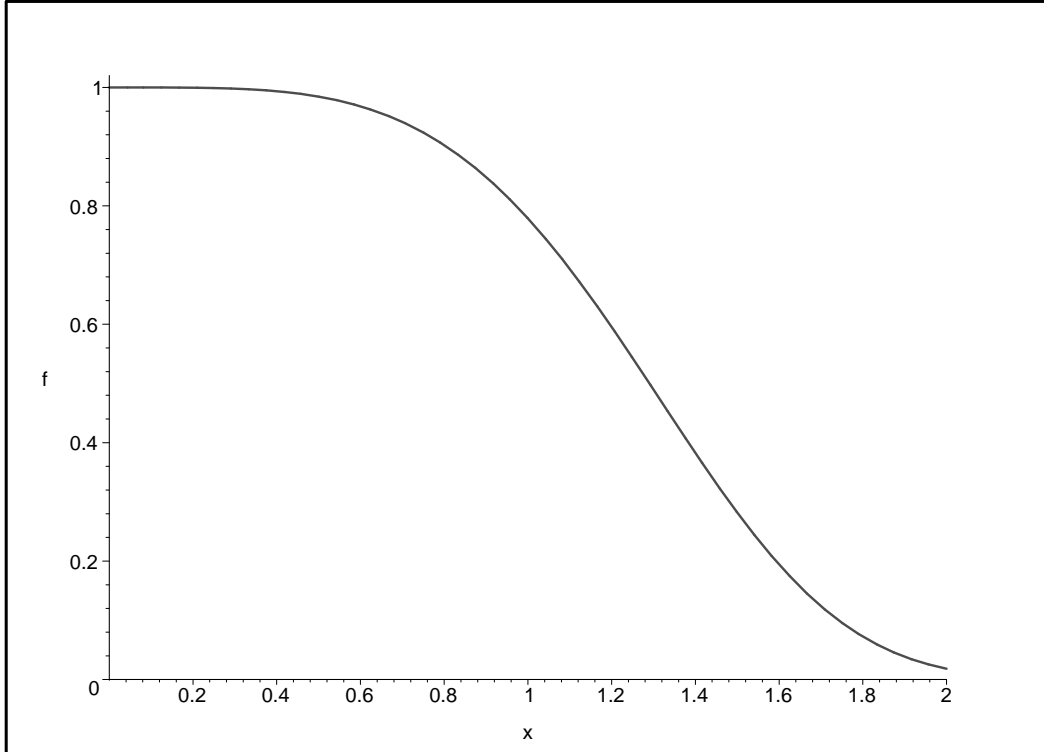

Figure 13: A form of approximation for size spectrum

the nucleation period stops.

Approximation (4) has rather high precision [2]. It is based on the following law of substance accumulation

$$G = z^4/4 = \int_0^z (z - x)^3 dx \equiv \int_0^z g(x)dx, \quad g = (z - x)^3 \equiv \rho^3$$

for the renormalized number G of molecules in a new phase. For any moment t or z a function g has one and the same form. We shall call this property as a "similarity of nucleation conditions". We see that every time the droplets formed at the last third of a period from beginning of nucleation until a current moment will accumulate a negligible quantity of substance. The relative quantity of the substance there has an order of ($\sim 1/27$) and is so small that even if there will be fluctuations the quantity will remain small.

From the form of f_1 it is seen that until $z_= \equiv 0.7z_0$ all droplets deplete vapor rather weak. It will be important for future analysis.

Another important property is the possibility to describe kinetics in frames of TAC with the help of monodisperce approximation (see [2]). The mentioned property of g allows to use a monodisperse approximation [2] not only at the end of nucleation but in every moment of the nucleation period [2]. Let $t(G)$ be the moment when there are G molecules in droplets (in appropriate units). An application of the monodisperse approximation [2] leads to

$$G \approx N_m(z)z^3$$

where $N_m(z)$ is the number of droplets born until $z/4$

$$N_m(z) = N(z/4) \approx z/4$$

and

$$N_m(z) \approx \frac{N(z)}{4}$$

for z which are essentially less than those corresponding the end of the nucleation period (in reality $z \leq z_=$.

4.2 Interaction of arbitrary stochastic fluctuations

The account of fluctuation interactions at every moment of time is important in justification of the smallness of stochastic corrections. Generally speaking, one can not take consideration only at the end of nucleation period without

justifications that the characteristic features of nucleation kinetics remains the same at every moment of time.

The arbitrary value of z in the period of nucleation corresponds to the arbitrary value of the number of droplets in a liquid phase G (in renormalized units which will be used (see [3]) the value G will belong to interval $(0, 1)$). Now it will be possible to repeat in some features the approach from [10] with arbitrary parameter G instead of 1 (in renormalized units, before renormalization it would be $1/\Gamma$ (see [3])). The sense of a difference from [10] is consideration of an arbitrary moment z instead of the end of nucleation. It is very important because allows to take into account all fluctuation effects during the nucleation period.

Let $t(z)$ be the current moment of time (z is the coordinate of the spectrum front, actually t is proportional z). We suppose that before az (a is some parameter) droplets are formed without mutual influence and one can write Poisson's distribution. This is the first group of droplets. The second group of droplets are all other droplets formed until the time moment z. A natural restriction on a appeared, namely $a < 0.7$. We shall take $a > 1 - 0.7 = 0.3$ also for the purposes explained below. We suppose that the influence of other droplets on its own formation is negligible (this follows from $2 * 0.7 = 1.4 > 1.25$ and from notation made above about the last third of nucleation period). Then it is possible to write Poisson's distribution for the second group of droplets, but with parameters depended on stochastic values - characteristics of the droplets distribution from the first group. Rigorously speaking one has to use the first four moments of the droplets distribution in accordance with [3], but for simplicity we shall use here only the zero momentum. As a compensation for this simplicity we has to use here only $a = 1/4$ which corresponds to the applicability of monodisperse approximation. But due to the arbitrary value of G this is quite sufficient for our goal.

Certainly, one can not state that precisely the first fourth of the spectrum plays the main role in vapor consumption. So, we have to consider interactions of stochastic fluctuations for all a which aren't too small in comparison with $1/4$ as well as $1 - a$ isn't too small in comparison with the same $1/4$. This will be done below.

At the next step of consideration one has to come from Poisson distributions to Gauss distributions and integrate them with account of connection between stochastic parameters of embryos formation from the first group and parameters of distribution from the second group. The same was done in [10]

34

but only for a leading term.

Why it is necessary to get all ascending terms in corrections? The existence of at least one coefficient with a big absolute value means (see the theory of Chebyshev polynomials) that there exist a size of a group where the interaction will lead to the big effect. Then it would lead that the interaction in these groups will be the real driving force of the process and these groups can be regarded as quasiparticles.

Contrary to [10] we shall take into account all correction terms which come from transition from Poisson's distributions to Gauss distributions and corrections for nonlinear connection between the group distributions. We shall take all terms which are growing when the total number of droplets grows.

We get the following result for droplets distribution

$$P = P_\infty(1+y)$$

where

$$P_\infty = (\frac{9a}{2\pi N(3a+1)})^{1/2}\exp(-\frac{9a}{3a+1}\frac{D_s^2}{2})$$

$$D_s = \frac{\hat{N}-N}{\sqrt{N}}$$

$\hat{N}$ - some stochastic value of the total number of droplets, N - the mean value of droplets and y is the correction for spectrum.

At $= 1/4$ we get

$$y = \frac{1}{74088}D_s(8087D_s^2 - 10269)s + (-\frac{4}{9} + \frac{305}{1176}D_s^2$$

$$-\frac{85903}{12446784}D_s^4 + \frac{65399569}{10978063488}D_s^6)s^2$$

where

$$s \equiv 1/\sqrt{N}$$

is a small parameter of decomposition. To get all ascending (with N) corrections we must fulfill decomposition until s^2.

Why it was necessary to get all ascending terms in decomposition? The answer lies in specific sequential influence which can be observed in nucleation period. The droplet appeared in the first moment of time forms condition for the embryos appearance in the second moment, then the embryos appeared

in the first and in the second moments form conditions for further appearance, etc. So, if there would be some N at which corrections will be big then immediately namely this value will be the crucial value for all kinetics. Fortunately here there is no such effect and, thus, we can take the theory with the averaged characteristics as the base for further constructions.

At arbitrary a we get for P/P_∞ (here P_∞ is the limit at $N = \infty$) the following expression

$$P/P_\infty = 1 + w_1 s + w_2 s^2$$

Here

$$w_1 = -\frac{1}{6}((486l^{12} + 486D_s^2 l^{12} - 972l^{11}D_s^2 + 324l^{10} - 648D_s^2 l^{10} + 756l^9$$

$$+810l^9 D_s^2 - 459l^8 + 297D_s^2 l^8 - 135l^7 D_s^2 -$$

$$387l^7 + 90l^6 D_s^2 - 153l^6 + 27l^5 D_s^2 - 213l^5 - 66l^4 D_s^2 - 3l^4 + 27l^3 - 3l^3 D_s^2 + 16l^2 D_s^2 - 3l^2 +$$

$$9l + lD_s^2 + D_s^2)D_s)/((1 + 3l^2)^3(l + 1)(-1 + l^2))$$

where

$$l = \sqrt{a}$$

and

$$w_2 = w_{02}/((l + 1)^2(-1 + l^2)(1 + 3l^2)^6 l^2)$$

$$w_{02} = \sum_{i=0}^{3} q_{2i} D_s^{2i}$$

$$q_0 = -\frac{1}{12} - \frac{1}{6}l + \frac{243}{4}l^{16} - \frac{135}{2}l^7 - 90l^8 - \frac{87}{2}l^6 + \frac{243}{2}l^{14} + \frac{81}{2}l^{12}$$

$$-\frac{153}{2}l^{10} - \frac{39}{2}l^5 - \frac{67}{6}l^4 - \frac{225}{2}l^9 - \frac{3}{2}l^2 - \frac{81}{2}l^{11} + \frac{243}{2}l^{13} - \frac{243}{2}l^{15} - \frac{17}{6}l^3$$

$$q_2 = \frac{5265}{4}l^{12} + \frac{51}{2}l^6 + 117l^{10} + \frac{333}{2}l^{11} + \frac{31}{8}l^4$$

$$+\frac{17}{2}l^5 + \frac{5049}{2}l^{14} - \frac{15309}{2}l^{19} + 2079l^{13}$$

$$+31l^8 - 8748l^{18} + 42l^9 + \frac{24057}{2}l^{21} + \frac{103}{2}l^7 + \frac{16767}{8}l^{20} + 6561l^{22}$$

$$+\frac{4617}{2}l^{15} - 3159l^{16} - 8262l^{17}$$

36

$$q_4 = -\frac{4413}{2}l^{13} - \frac{477}{2}l^{15} + 7047l^{21} - \frac{1161}{4}l^{18}$$

$$+\frac{361}{6}l^8 + \frac{105}{2}l^{11} - \frac{104247}{4}l^{22} - \frac{3}{4}l^4 + 17091l^{20}$$

$$-5103l^{23} + \frac{43}{6}l^5 - \frac{31185}{4}l^{19} + 7965l^{17} - \frac{3213}{4}l^{12} - \frac{475}{3}l^{10} + 510l^{14} - \frac{49}{6}l^7 + \frac{23}{4}l^6$$

$$+\frac{1}{12}l^3 + \frac{44469}{4}l^{24} - \frac{1}{12}l^2 - \frac{6903}{4}l^{16} + \frac{74}{3}l^9$$

$$q_6 = -13122l^{25} - \frac{40419}{8}l^{18} + \frac{17253}{2}l^{20} - \frac{24057}{2}l^{22} + 4374l^{24} + \frac{6561}{2}l^{26} -$$

$$\frac{48843}{2}l^{21} - \frac{623}{24}l^8 + \frac{59}{36}l^6 - \frac{3609}{4}l^{14}$$

$$-\frac{57}{8}l^{12} + \frac{411}{4}l^{10} + \frac{11}{24}l^4 + \frac{1}{72}l^2 - \frac{29}{12}l^7 - \frac{345}{4}l^{11} + \frac{1}{36}l^3 +$$

$$\frac{13}{36}l^5 + \frac{65}{4}l^9 + \frac{2421}{4}l^{13} - \frac{7857}{4}l^{15} +$$

$$\frac{8667}{4}l^{17} + 28431l^{23} + 7047l^{19} + \frac{24705}{8}l^{16}$$

Having integrated this expression we get corrections to droplets number. The term at s gives zero after integration and the first non zero correction has an order of $\sim s^2$ and doesn't depend on the total number of droplets. A coefficient at s^2 has at $a = 1/4$ a value

$$d_0 = 311/3024 \ll 1$$

At arbitrary a a coefficient at s^2 in correction for the total number of droplets will be

$$d_a = \frac{1}{72}[108a^6 + 540a^{11/2} - 72a^5 - 930a^{9/2} - 336a^4 +$$

$$713a^{7/2} + 158a^3 + 4a^2 - 203a^{5/2} - 6a + 39a^{3/2} - 3a^{1/2}]/[a^{3/2}(1-a)^2(1+3a)]$$

It will be interesting to compare results with and without corrections from transition from Poisson's distribution to Gauss distribution. So, we consider now this case. At the leading term there will be no change. At correction terms we have

$$y = -\frac{17}{74088}D_s(-2331 + 289D_s^2)s + (\frac{17}{196}D_s^2 +$$

$$\frac{732037}{12446784}D_s^4 + \frac{24137569}{10978063488}D_s^6 - \frac{13}{36})s^2$$

$$d_0 = -37/126$$

$$d_a = \frac{1}{72}(648a^{11/2} - 216a^5 - 1062a^{9/2} + 108a^4 + 753a^{7/2} -$$

$$30a^3 - 195a^{5/2} - 12a^2 + 19a^{3/2} + 6a - 7a^{1/2})/(a^{3/2}(1+3a)(1-a)^2)$$

It is seen that these corrections are small. At arbitrary a except too small ones and those close to 1 (these values are unreal) we get values shown at fig.14
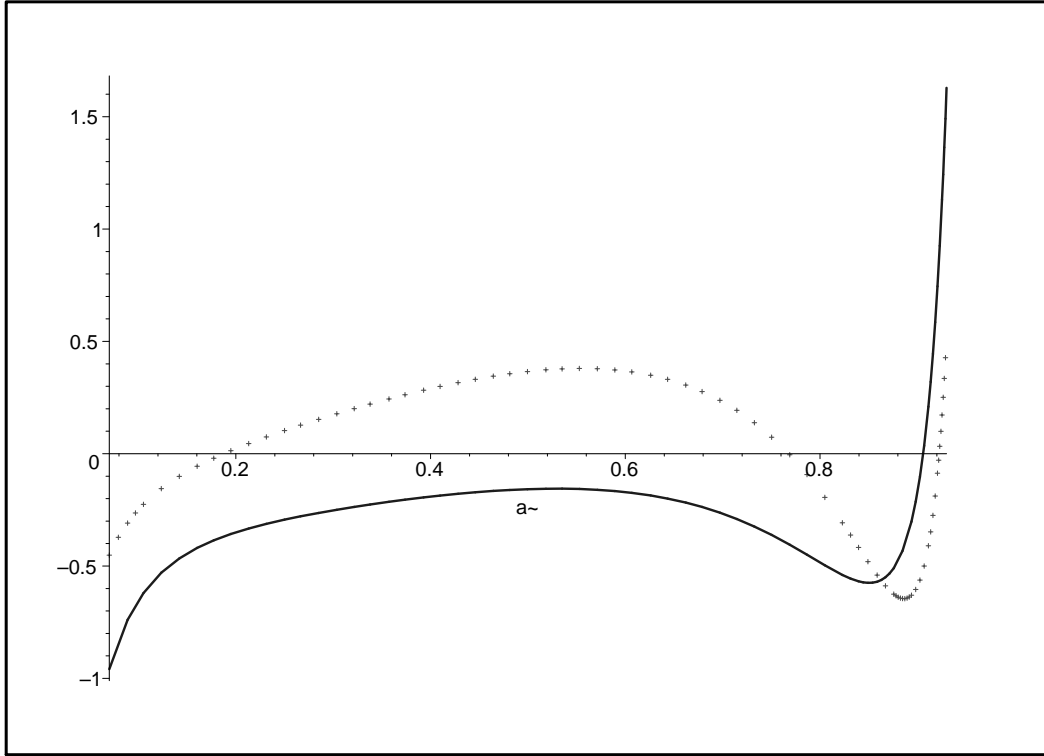

Figure 14: Dependence of corrections, i.e. of d_a on a

A point curve shows corrections with transition from Poisson's distribution to Gauss distribution taken into account, a line shows corrections without transition from Poisson's distribution to Gauss distribution. Both corrections have one and the same order and they are small.

We see the plateau for all a except $a \ll 1/4$ and $1-a \ll 1/4$. So, here the smallness of corrections due to the interactions of stochastic peaks is quite clear.

But still the small value of corrections can lead through sequential influence to essential change of the total droplets number. Conclusion about the smallness of correction in the total number of droplets can be made on the base of specific kinetic features of the process (see "the effect of the first droplet") which will be done later.

One has to note that we have not taken into account corrections from transition from summation to integration. This is definitely required by discrete character of droplets number. It is made due to reasons formulated below. Really, we have at transition from summation in formula

$$P(N) = \sum_{\hat{N}_1} P_1(\hat{N}_1, N_1) P_2(N - \hat{N}_1 - \hat{N}_2, N_2(\hat{N}_1))$$

to integration[5]

$$P(N) = \int d\hat{N}_1 P_1(\hat{N}_1, N_1) P_2(N - \hat{N}_1 - \hat{N}_2, N_2(\hat{N}_1))$$

to use the Euler-McLorrain's decomposition. It brings to asymptotic serial, which can be included into a final answer.

This is the formal solution of the problem. But discrete character in nucleation isn't so trivial. The process of vapor consumption can not begin without the first droplet. The system will wait for droplet as long as it will be necessary. It shows that discrete effects are complicate and require a separate publication. At least one has to put the initial moment at the moment of the first droplet appearance and then to consider condensation with the substance in the first droplet calculated explicitly as $\sim z^3$

This property will be called as "the effect of the first droplet". Here it leads only to the small effects, but in the situation of smooth variation of external conditions the effect can be greater.

---

[5]Here N is the total number of droplets, $\hat{N}_1$ is the stochastic number of droplets in the first group, $\hat{N}_2$ is the stochastic number of droplets in the second group, N_1 is the mean number of droplets in the first group, N_2 is the mean number of droplets in the first group, which is a function of $\hat{N}_1$. The value N remains stochastic number.

4.3 Self similarity of Gaussians

To use Poisson's distribution for the first group of droplets one has to make the following notation. Really nucleation conditions for the first group don't differ from the whole group. So, for distribution for the first group one has to take distribution P_1 with reduced half-width. But one can not attribute a half-width to Poisson's distribution. That's why we considered effects with and without corrections from transition from Poisson's to Gauss distribution. So, we can use Gauss distributions as initial ones. For Gauss distribution one can easily reconsider the half-width. Then for P_1 one can take

$$P_1 \sim \exp(-(\hat{N}_1 - N_1)^2/(2bN_1))$$

where b is a renormalization coefficient. Distribution P_2 remains previous

$$P_2 \sim \exp(-(\hat{N}_2 - N_2)^2/(2N_2))$$

where N_2 is given by

$$N_2 = (1 - \frac{1}{3}s + \frac{2}{9}s^2 - \frac{14}{81}s^3 + \frac{35}{243}s^4 - \frac{91}{729}s^5 - a)N$$

where N is a mean total number of droplets,

$$s = \frac{\hat{N}_1 - aN}{aN}$$

is a small parameter of an order $N^{-1/2}$

After integration one comes to

$$P \sim \exp(-\frac{9a}{2(9a + b - 6ba + 9ba^2 - 9a^2)}d^2)$$

where

$$d = (\hat{N} - N)/\sqrt{N}$$

The half-width of the distribution P_1 must be equal to the half-width of P, which leads to

$$b = 9\frac{a(1-a)}{-9a^2 + 15a - 1} \tag{5}$$
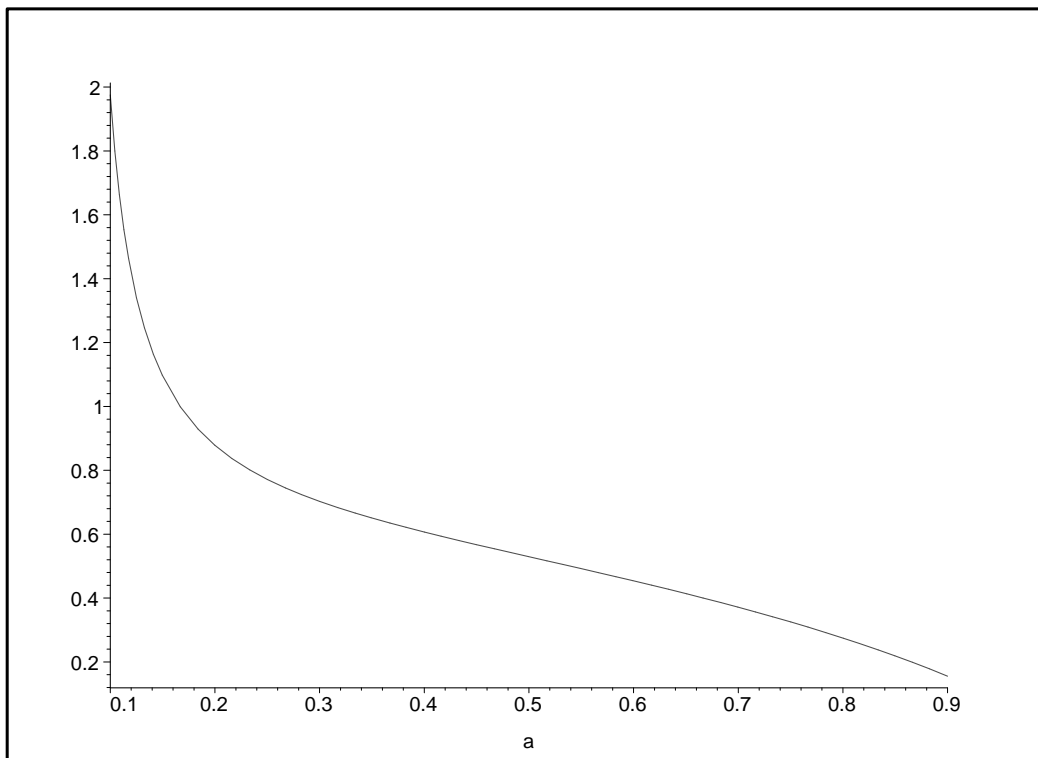
This value is drawn in fig. 15.

Figure 15: Function $b(a)$.

Now we shall consider effects of renormalization. The ratio of corrections with renormalization and without renormalizations is given by

$$r = \frac{1}{9} \frac{\sqrt{-9a^2 + 15a - 1}\sqrt{3a + 1}}{a\sqrt{1 - a}}$$

and it is shown at fig. 16

For all reasonable values of a the last ratio is approximately 1. At $a = 1/4$ we get 1.0041 Here the effect of similarity of nucleation conditions doesn't lead to remarkable effects in the change of half-width. But here the smallness of change takes place only because of application of monodisperse approximation and later this change will be essential.

Instead of taking into account all moments of distribution we can directly calculate the effects on the base of explicit form of spectrum in frames of iteration procedure.

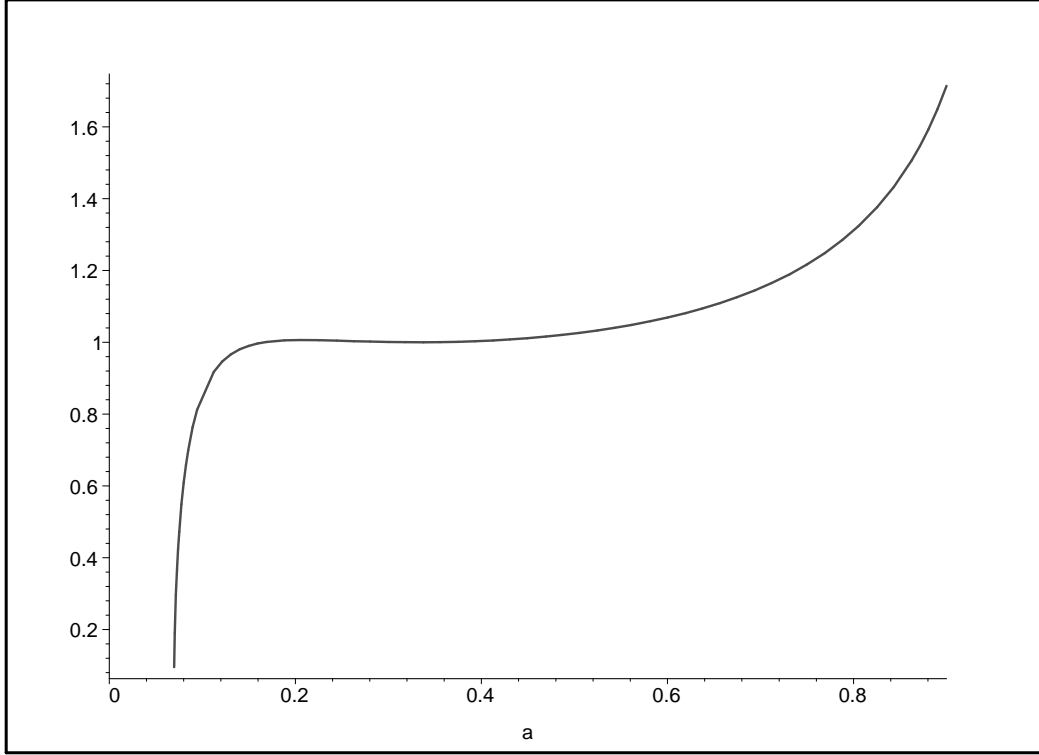The result of the previous consideration is the following: we have proved

Figure 16: Ratio of halfwidths

that stochastic effects are small. Beside this we have demonstrated how to use the similarity of nucleation conditions. Here it doesn't lead to any remarkable effect, but later under the smooth external conditions this method will lead to some essential numerical corrections.

One has to stress that in [1] a linearization over deviation of the droplets number from the mean value was made. It was necessary to perform calculations. But in the linear theory one can not get the deviation of the mean value of result from the value calculated on the base of averaged characteristics. So, the attempt to get deviations in the mean value of droplets in [1] is senseless.

4.4   Calculation of dispersion

Since the mentioned combination of gaussians is also a gaussian characterized by a mean value and by a dispersion one has to determine these values for

the distribution of the total number of droplets. As it was shown above the mean value of the droplets number is practically the same as it is prescribed by TAC and we are interested in dispersion. Now we shall calculate this value properly.

The most advanced approach to solve this problem[6] was suggested in [1]. But even this approach has many disadvantages and we need to reconsider it.

We shall characterize a droplet by a linear size ρ which is the cubic root of its molecules number. Its velocity of growth at fixed supersaturation does not depend on ρ.

Decomposition of a whole interval of nucleation into elementary intervals is connected with some difficulties. An elementary length $\tilde{\Delta}$ according to [1] must satisfy two requirements:

1. A number of droplets formed during elementary length must be great.

2. An amplitude of a spectrum has to be approximately constant during an elementary interval.

It is clear that the second requirement can not be satisfied. Stochastic deviations of an amplitude leads to the violation of the second requirement.

We shall apply the second requirement not to the stochastic amplitude as it was stated in [1], but to the averaged amplitude. Then the second requirement is:

An averaged amplitude of a spectrum has to be approximately constant during an elementary interval.

Now we shall see the evident illegal consequences of the approach from [1]. "Stochastic" amplitudes f_i are introduced in [1] as

$$f_i = \frac{N_i}{\tilde{\Delta}}$$

where N_i is the number of droplets formed during $\tilde{\Delta}$. It isn't the height of spectrum but simply the renormalized value of the droplets number appeared during this interval. An expression for the number of molecules in droplets formed during interval number i at a moment t_k (or z_k) (it means that now we are at interval number k) with approximately constant rate of nucleation

---

[6]Certainly, already expression (5) gives the decrease of the Gaussian halfwidth and can lead directly to dispersion where b is smaller than a standard one. But b essentially depends on a. For $0.2 \leq a \leq 0.9$ one can see the approximate formula $b = 0.6 - (a - 0.5)\frac{0.7-0.2}{0.9-0.3}$ and the absence of concrete value for a doesn't allow to get a concrete value for b.

$\bar{f}_i$ would be the following one

$$\int_{x_{k-i}}^{x_{k-i+1}} \bar{f}_i \rho^3 d\rho = \frac{1}{4} \bar{f}_i (x_{k-i+1}^4 - x_{k-i}^4)$$

Namely, this equation was derived in [1] and forms the base of further consideration. Here x_{k-i} is the coordinate ρ of the droplet which was born at z_i at a moment z_k (it corresponds to the definition $x = z - \rho$) The difference between forth powers corresponds to a constant amplitude of spectrum. It is wrong and then eq. (12) in [1] and all further equations are not correct.

But the is no necessity to use such a way to make an account of the number of molecules in a new phase. It is absolutely sufficient to take the following expression

$$\int_{x_{k-i}}^{x_{k-i+1}} \bar{f}_i \rho^3 d\rho = N_i x_{k-i}^3 \approx N_i x_{k-i+1}^3$$

which is valid at $k - i \gg 1$. In a whole quantity of substance it is sufficient to take into account only droplets with $k - i \gg 1$. The relative weight of dismissed terms will be small.

Then for the total number of molecules in droplets at interval number k we have the following expression

$$Q_k = \sum_{i=1}^{k} N_i x_{k-i}^3$$

where x_{k-i} is a corresponding coordinate. This expression can be rewritten as

$$Q_k \sim \sum_{i=1}^{k} N_i \hat{\Delta}^3 (k-i)^3$$

This representation is important because now the note in [1] after eq. (15) isn't necessary. That note stated that the probability for N_i to deviate from the number $\bar{N}_i$ of droplets calculated in TAC under the supersaturation formed by stochastically appeared droplets in previous intervals is very low. That note is doubtful because namely these deviations are the base for stochastic effects. Now there is no need in this note.

The next step is to build [1] a two cycle construction for nucleation period. During the first cycle the main consumers of vapor appeared in a system and during the second cycle they govern a process of formation of all other

droplets. In [1] it is supposed that during the first cycle a vapor depletion is negligible and during the second cycle new droplets are absolutely governed by droplets from the first cycle. Now we shall analyze an effectiveness of such procedure.

In TAC the corresponding evolution equation will be

$$\psi(z) = \int_0^z (z-x)^3 \exp(-\psi(x))dx$$

The first iteration [3] is practically a precise solution and it gives the number of droplets

$$N_{tot} = \frac{1}{4} \frac{4^{1/4}\pi\sqrt{2}}{\Gamma(3/4)} = 1.2818$$

A model solution requires that until $z = p$ there will be no depletion of vapor and then only the droplets formed before $z = p$ will consume vapor. Then for a total number of droplets we have an expression

$$N_{tot\ appr} = p + \int_p^\infty \exp(-\frac{1}{4}x^4 + \frac{1}{4}(x-p)^4)dx$$

A ratio $q = N_{tot\ appr}/N_{tot}$ is given in fig. 17

Always $N_{tot\ appr}$ is greater than N_{tot}. The value of minimum corresponds to $p \sim 0.78$ which is 55 percent of the total length of spectrum. We can stress the smooth dependence $N_{tot\ appr}$ on p.

It is clear that in [1] the value of parameter of separation into two cycles was not chosen in a good style (at least from the point of view of TAC). It corresponds to $p = 0.64$.

Now we shall study the probability P_k of formation of stochastic number N_k of droplets at the first k elementary intervals. Our constructions now resemble [1] but there is one essential difference. We have no necessity to linearize expression with respect to $(N_i - \bar{N}_i)/\bar{N}_i$, where N_i is a stochastic number of droplets formed at interval i, $\bar{N}_i$ is a mean number of droplets formed at interval i (it is a function of stochastic numbers of droplets at preceding intervals). This linearization can not take place because a ratio $(N_i - \bar{N}_i)/\bar{N}_i$ can be zero or can attain huge value (with a low probability). It is more simple and more justified to linearize expression on $\sum_i \rho_i^3 (N_i - \bar{N}_i)/\bar{N}_i$ where ρ_i is a linear size of droplets formed at interval i (all of them have approximately the same size). Really, due to summation the relative variations of $\sum_i \rho_i^3 (N_i - \bar{N}_i)/\bar{N}_i$ are much smaller than variations of $(N_i - \bar{N}_i)/\bar{N}_i$.
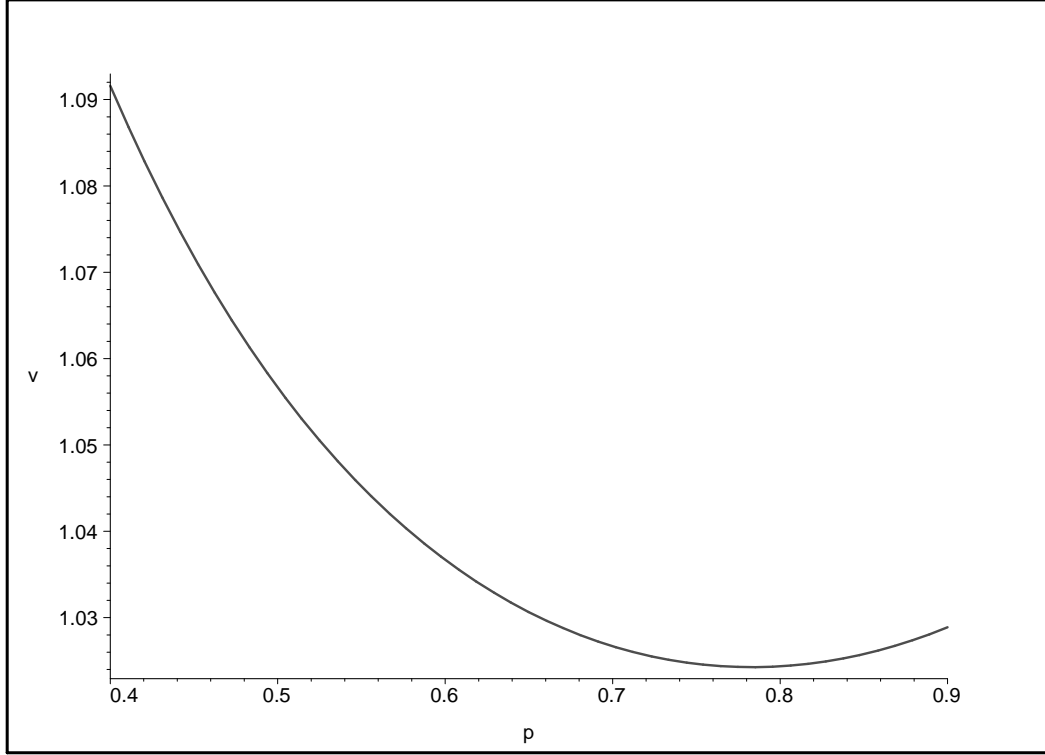
Figure 17: The ratio of mean numbers of droplets

Variations of $(N_i - \bar{N}_i)/\bar{N}_i$ would be small only at very big numbers of droplets N_{tot}. One can get

$$(N_i - \bar{N}_i)/\bar{N}_i \sim \bar{N}_i^{-1/2}$$

$$N_{tot} \sim M\bar{N}_i$$

M is a number of elementary intervals. So, the theory with linearization proposed in [1] would be well justified only in a region where the result can be obtained on the base of averaged characteristics. The internal contradiction between the big number M and the smallness of fluctuations in the elementary interval in [1] is obvious.

The linearization proposed here is much more weak than in [1]. But it leads to the analogous numerical expressions as in [1]. So, restrictions from [1] are not necessary.

For dispersion of the total distribution the result proposed in [1] was the

following
$$D^\infty = \tilde{N}^\infty(1 - \frac{\beta}{\alpha})$$

where
$$\beta = \beta_1 - \beta_2$$

$$\beta_1 = 8 \int_{1/2}^{\infty} d\xi \int_0^{1/2} d\tau (\xi - \tau)^3 \exp(-\xi^4)$$

$$\beta_2 = 16 \int_{1/2}^{\infty} d\xi \int_{1/2}^{\infty} d\eta \int_0^{1/2} d\tau (\tau - \xi)^3 (\tau - \eta)^3 \exp(-\xi^4) \exp(-\eta^4)$$

$$\alpha = \int_0^{\infty} dx \exp(-x^4)$$

In the two-cycles construction the value of α, which is proportional to the total number of droplets has to be reconsidered and recalculated on the base of two cycles. Then we have to use instead of previous $\alpha \equiv \alpha_0$ a new value

$$\alpha = \alpha_1 \equiv 1/2 + \int_{1/2}^{\infty} \exp(-x^4 + (x - 1/2)^4) dx$$

In our approach we shall use parameter k of separation[7] of two cycles and we shall calculate α_1 as

$$\alpha_1 \equiv k + \int_k^{\infty} \exp(-x^4 + (x - k)^4) dx$$

Then according to fig. 17 we see that the ratio α_0/α_1 is greater than 1 and α_1 is greater than α_0. Here we see that two-cycles construction is approximate one. Then result for D^∞ will differ from the number published in [1] and will be (here one has to put $k = 1/2$)

$$D_e^\infty = \tilde{N}^\infty 0.69$$

instead of
$$D_f^\infty = \tilde{N}^\infty 0.67$$

as it is written in [1].

Numerical simulations show that the value D_e^∞ is one tenth more than a real result. So, the new theory is necessary.

---

[7]Here for simplicity we use k instead of $p/4^{1/4}$.

Now it is necessary to decide what k shall we choose. At arbitrary k the expression for β will be the same but for β_1 β_2 we have

$$\beta_1 = 8 \int_k^\infty d\xi \int_0^k d\tau (\xi - \tau)^3 \exp(-\xi^4)$$

$$\beta_2 = 16 \int_k^\infty d\xi \int_k^\infty d\eta \int_0^k d\tau (\tau - \xi)^3 (\tau - \eta)^3 \exp(-\xi^4) \exp(-\eta^4)$$

We have also to reconsider expression for α.

After calculations we have for dispersion as function of k the following fig. 18
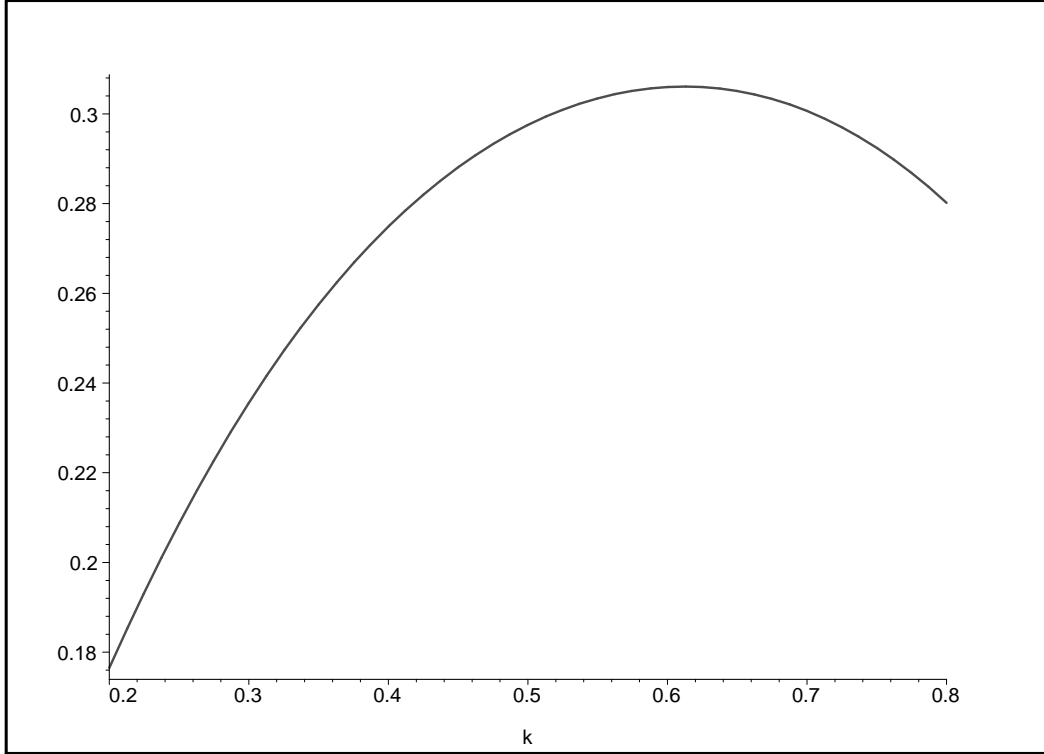

Figure 18: Relative deviation in dispersion as function of k

A minimal dispersion will be at $k = 0.6$. This value approximately equals to $k = 0.55$ which ensures minimum of α_1 where the result is the most close to the real value in the number of droplets. One can also add that this is the true value of k because namely this value corresponds to the sense of minimal work when we have the low dispersion. It corresponds to a minimal (in a

48

certain sense) entropy and later we can get additional work from increase of entropy.

Dispersion at $k = 0.6$ will be

$$D^\infty = 2\tilde{N}^\infty 0.66$$

Now we shall calculate the value of dispersion more accurate. Due to the similarity of nucleation the first cycle doesn't differ from the whole period. Function β for the first cycle will be

$$\beta = \beta_1 - \beta_2$$

$$\beta_1 = 8 \int_{k_1}^{k} d\xi \int_{0}^{k_1} d\tau (\xi - \tau)^3 \exp(-\xi^4)$$

$$\beta_2 = 16 \int_{k_1}^{k} d\xi \int_{k_1}^{k} d\eta \int_{0}^{k_1} d\tau (\tau - \xi)^3 (\tau - \eta)^3 \exp(-\xi^4) \exp(-\eta^4)$$

Calculations for $k_1 = 0.6 * 0.6 = 0.36$ and $k = 0.6$ give $\beta = \beta' \equiv 0.0255$.

In the most rough approximation one has to add $\beta' = 0.0255$ to the previous value of $\beta = 0.305$ which leads to $\beta = 0.32 \div 0.33$. The smallness of β' in comparison with β allows to use this linear approximation. For this value of β the value of dispersion will be

$$D^\infty = D_3^\infty \equiv 2\tilde{N}^\infty 0.64$$

It is interesting that this result can be gotten by another (rather artificial) procedure:

We suppose that β_1 and β_2 are the first two terms of some series. We don't know other terms, but it is reasonable to suppose that the series resembles geometric progression with denominator β_2/β_1. This leads to dispersion

$$D^\infty = 2\tilde{N}^\infty 0.64107$$

As it follows from fig.19 the value of extremum remains $k = 0.6$.

The absence of the shift of extremum is important and is necessary for this approach to be a self consistent.

Now we shall see whether some other approaches can lead to essential reconsideration of result for dispersion.

A way to make results more precise is take into account the shift of dispersion directly in initial formulas. Having written for the dispersion correction in the first cycle
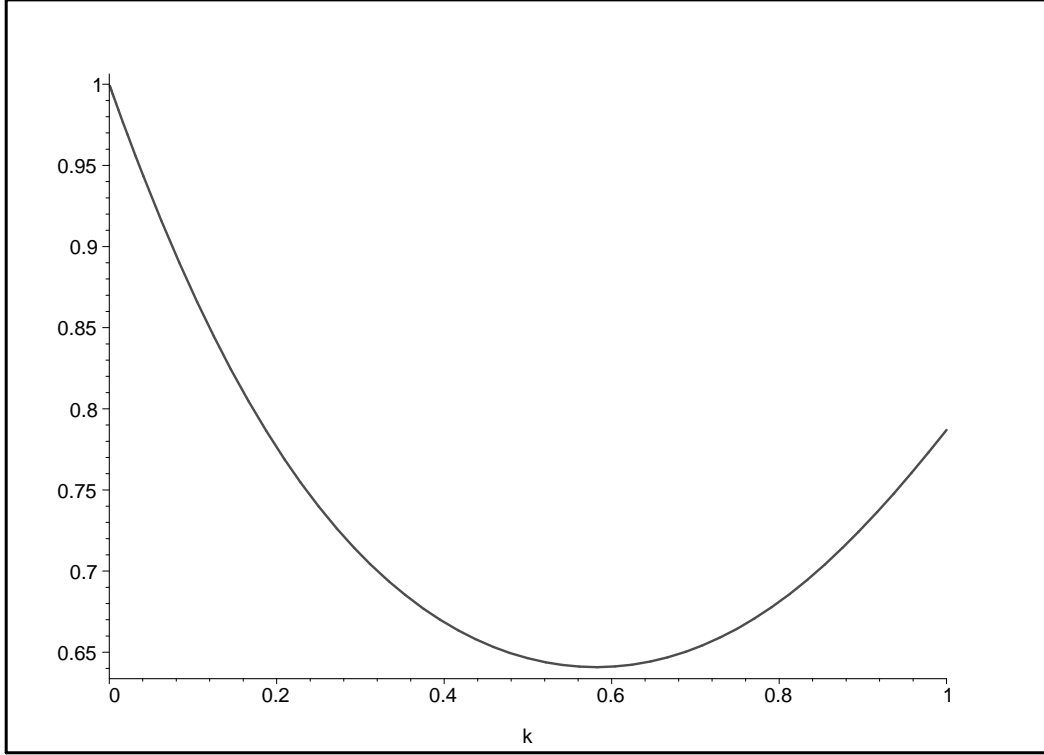
$$D_3^\infty = 2\tilde{N}^\infty \gamma$$

Figure 19: Dispersion.

with parameter γ, we get for the final distribution

$$P^{(k)} \sim \int_{-\infty}^{\infty} dN_1 dN_2...dN_P \prod_{i=1}^{P} \exp(-\frac{(N_i - \bar{N}_1)^2}{2\gamma \bar{N}_1})$$

$$\exp[\frac{[N^{(k)} - N^{\tilde{(k)}} - \sum_{j=1}^{P} a_j^{(k)}(N_j - \bar{N}_1)]^2}{2(N^{\tilde{(k)}} - P\bar{N}_1)}]$$

where P is the number of elementary intervals until the argument k, $N^{\tilde{(k)}}$ is the number of droplets calculated on the base of the theory with averaged characteristics, $\bar{N}_i$ the mean number of droplets formed during interval number i with account of fluctuations from previous intervals. The values $a_i^{(k)}$ are given by

$$a_i^{(k)} = 1 - \sum_{j=P+1}^{k} \frac{\exp(-j^4/M^4)}{M^4} 4(j-i)^3$$

50

and M is the total number of intervals.

Having fulfilled integration $\int_{-\infty}^{\infty} dN_1 dN_2 ... dN_P$, we get for a limit value of dispersion

$$D^\infty = 2\tilde{N}^\infty (1 - \frac{k(1-\gamma)}{\alpha} - \frac{\gamma\beta}{\alpha})$$

The approximate similarity of spectrums leads to equation on γ, which can be easily solved

$$\gamma = \frac{1 - \frac{k}{\alpha}}{1 + \frac{\beta}{\alpha} - \frac{k}{\alpha}}$$

Calculations lead to

$$\gamma(k = 0.6) = 0.51$$

This result is very strange. It radically differs from the previous one. Certainly we made an error. The reason of the error in previous approach is that the duration of the first cycle is limited by k. So, we have to limit the duration of a whole period. The limit of the whole nucleation is, evidently, ~ 1.

The limit of integration corresponds to the current moment of time. It can not be greater than 1. So, we have to take it equal to 1. Then we have to recalculate β as

$$\beta_{initial} = \beta_1 - \beta_2$$

$$\beta_1 = 8 \int_k^1 d\xi \int_0^k d\tau (\xi - \tau)^3 \exp(-\xi^4)$$

$$\beta_2 = 16 \int_k^1 d\xi \int_k^1 d\eta \int_0^k d\tau (\tau - \xi)^3 (\tau - \eta)^3 \exp(-\xi^4) \exp(-\eta^4)$$

To calculate the value of dispersion we can act in two manners. The first way is to calculate dispersion at the point of extremum of β. Now we shall show a dependence $\beta_{initial}$ on k at fig. 20.

Calculations give $\beta_{initial} = 0.18$ and for the final dispersion

$$D_3^\infty = 2\tilde{N}^\infty 0.65$$

This value practically coincides with a previous approach.

It is necessary to stress that one can not directly use extremal properties of γ to get p which provides β extremum. In reality the final characteristic is γ, but the calculations show that γ has no extremum. Certainly, this is the weak point of approach based on extremal properties.
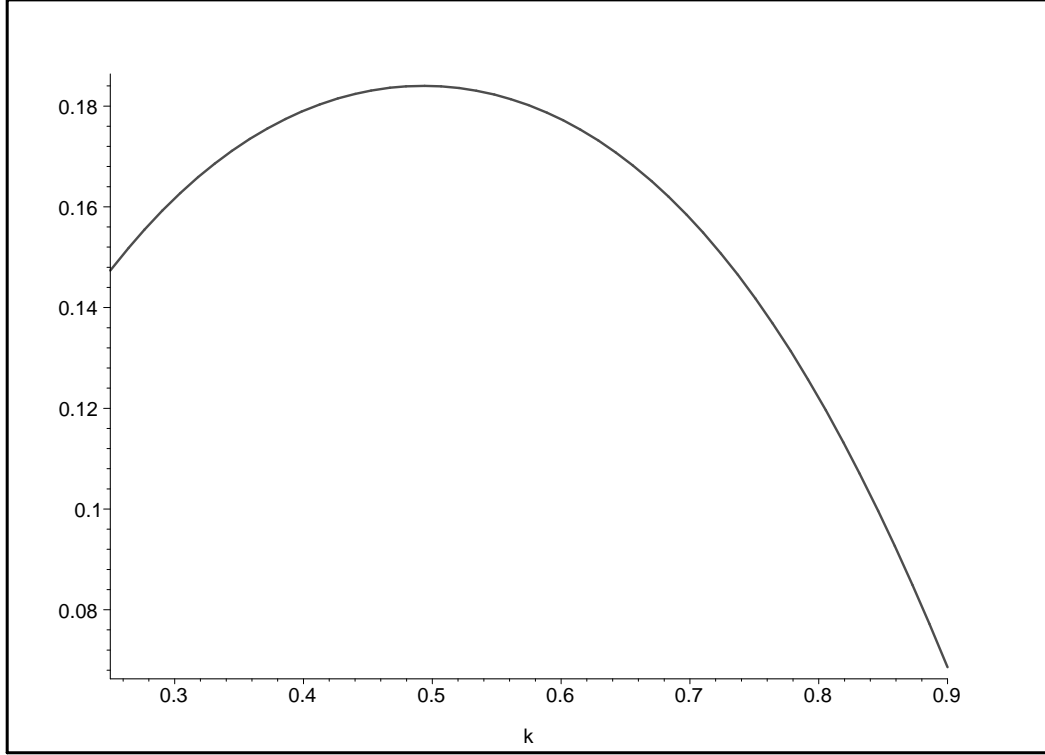
Figure 20: $\beta_{initial}$ as a function of k

Another way is to use k which provides the most precise value for the total number of droplets in this model. Having compared the mean total number of droplets in TAC calculated in this model one can see that this number has minimum 0.927 which is greater than the precise value and the value 0.90 given in the first iteration. This extremum is attained at $k = 0.55$. Namely this value will be chosen as k and this leads to

$$D_4^\infty = 0.62$$

which lies in frames of precision of numerical simulation.

One can add that there is no need to use k corresponding to extremum of the number of droplets calculated up to 1 instead of ∞. Then the minimum is 0.852 and it is attained at $k = 0.45$. Actually there is no reasons to take this value because here the value of minimum is strongly less than the precise value and it corresponds to the maximum of deviation from the precise value. So, there are no reasons to take this value.

One has to stress that the procedure adopted here is really necessary. The two-period model with a fixed boundary in time scale used in [1] can not be the base of the correct calculation of dispersion. The reasons are the following

- The behavior of supersaturation here is the model behavior (MB) with parameters, which characterize the influence of the first part of spectrum. In investigation of stochastic effects the fluctuations of these parameters are the source of fluctuations of the total number of droplets. The fuctional form of MB is chosen to ensure the correct number of droplets in frames of TAC. The change of parameters in MB leads to the imaginary change of external conditions in TAC which corresponds to the MB with given parameters.

- The change of external parameters in TAC has to lead to the change of the boundary between parts. But this can not be done in the model with a fixed boundary.

In our approach the summation of geometric progression and all other approaches ensure the possibility to overcome the restrictions of the two parts approach with a fixed boundary. The summation of geometric progression describes the equivalence of all points which is prescribed by the property of similarity of spectrums.

The relative smallness of numerical errors in [1] is caused by the following reasons

- The moderate possibility of linearization (the non-linearity isn't too big) in kinetics of decay

- The weak dependence N_{tot} on p in frames of TAC

- The weak dependence of N_{tot} on $N(p)$ in frames of TAC

- The effects of stabilization are very strong. Really, instead of addition 0.5 the benefit of the second part to dispersion is only $0.64 - 0.5 = 0.14$ (or even less if we use $p \sim 0.55$ instead of $p \sim 0.5$)

- The existence of the special buffer part of nucleation period which will be described later

4.5 Numerical results

Numerical simulation of nucleation can be done by the following method. We split the nucleation interval into many parts (steps). At every step a droplet will be formed or not. The probability to appear must be rather low, then we ensure the smallness of probability to have two droplets at the same interval. This means that the interval is "elementary".

The process of formation is simulated by a random generator in a range $[0, 1]$. If a generated number is smaller than a threshold parameter u, then there will be no formation of a droplet. If it is greater than a threshold, we shall form a droplet. As a result we have spectrum $\hat{f}$ of droplets sizes. Now it is a chain of 0 and 1. The parameter u descends according to macroscopic law [3]

$$u = u_0 \exp(-\Gamma G/\Phi)$$

from a theory with averaged characteristics (it is based only on a conservation law without any averaging and can be used). Here

$$\Gamma \sim \frac{dF_c}{d\Phi} \sim \nu_c \tag{6}$$

Φ is the initial supersaturation, F_c is a free energy of critical embryos formation, ν_c is a number of molecules inside a critical embryo, G is the number of molecules in a new phase taken in units of a molecules number density in a saturated vapor. By renormalization one can take away all parameters except G.

To simplify calculations radically one can use the following representation [3] for G:

$$G = z^3 G_0 - 3z^2 G_1 + 3z G_2 - G_3$$

where z is a coordinate of a front of spectrum, and G_i are given by

$$G_i = \int_0^z \hat{f}(x) x^i dx$$

We needn't to recalculate G_i, but can only ascend the region of integration, having added to integrals the functions $z^i \hat{f}(z) dx$ at every step.

Our results are given below. The interval is split into 30000 parts. Parameter u_0 have been varied from 0 up to 1 which leads to a different number of droplets. It is clear that the limit values are not good: at 0 there are no droplets in the system, at 1 our intervals are not elementary. At every u_0 results were averaged over 1000 attempts.
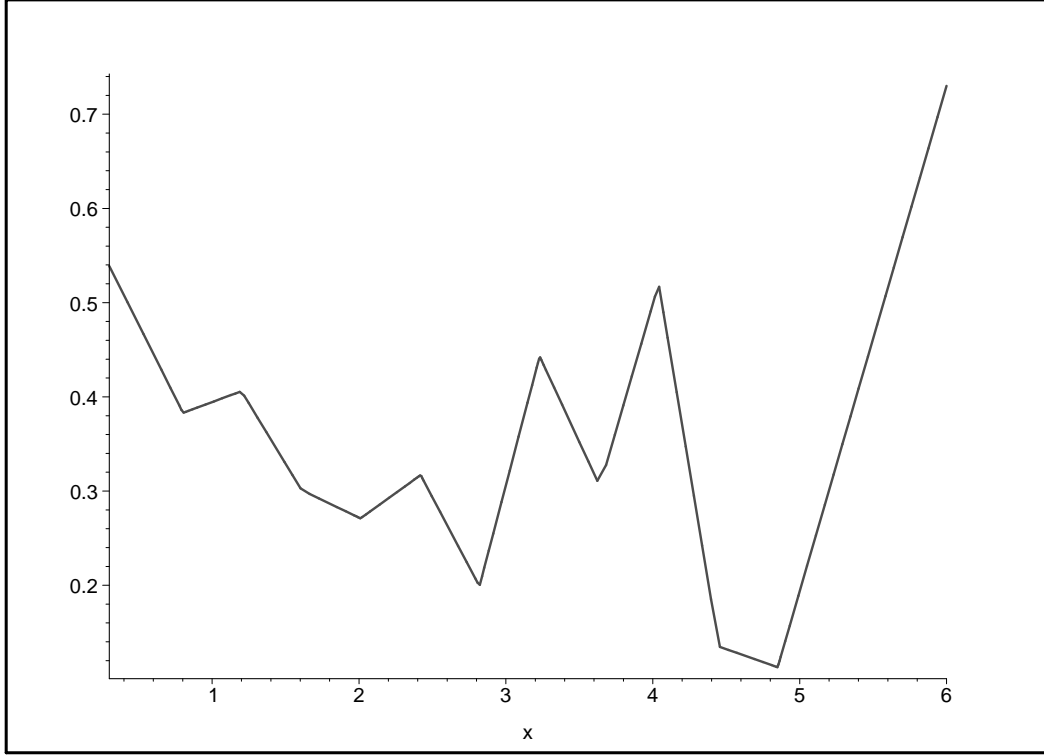
Figure 21: Shifts of droplets numbers as a function of $\ln N^{\widetilde{(\infty)}}$

Shifts of droplets numbers are drawn at fig.21 as a function of $\ln N^{\widetilde{(\infty)}}$

It is seen that an analytical result about negligible value of corrections is correct.

Dispersion as a function of $\ln N^{\widetilde{(\infty)}}$ is shown in fig. 22.

It is seen that the analytical value of dispersion coincides with numerical simulation. The ends of the curve correspond to a zero number of droplets and to a giant number of droplets when the elementary intervals are not elementary and have to be thrown out.

Stochastic effects in dynamic conditions [3] can be analyzed by the same method. We needn't to describe it here. Numerical results are drawn below. Fig. 23 shows the shift in the number of droplets. It is small. Dispersion is drawn in fig. 24 (i.e. the value of γ). It is greater than in the case of decay.

The physical reasons for the smallness of the droplet number shift for decay and for dynamic conditions will be different.

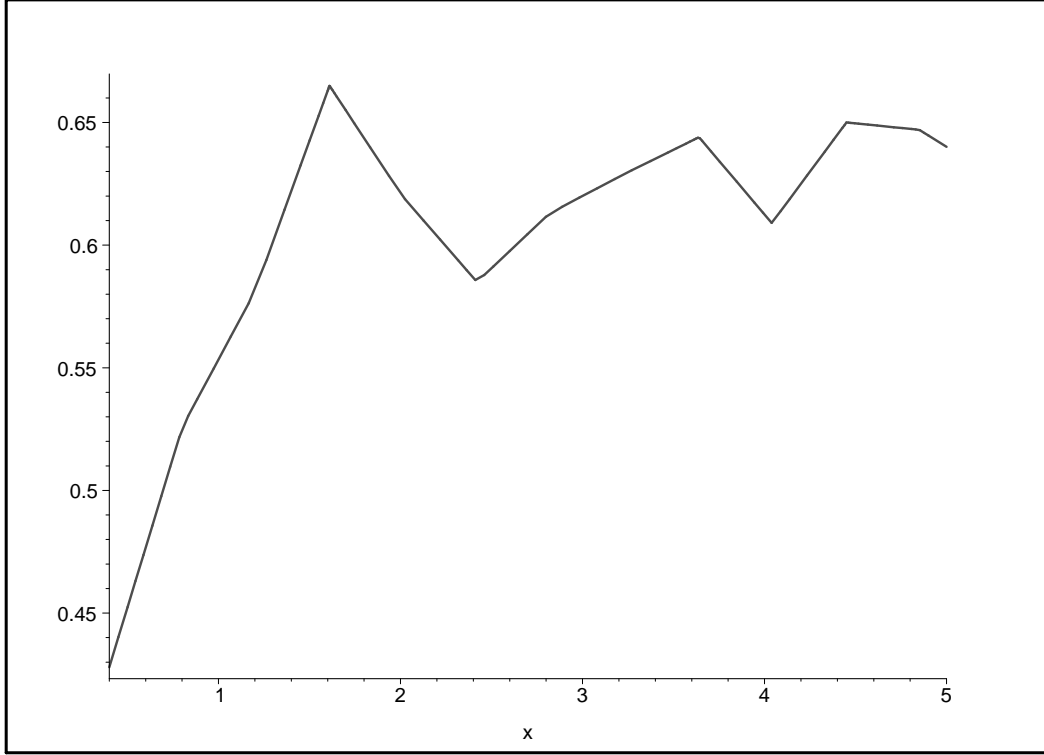For decay the reason is the following. The system wait the first droplet

Figure 22: Relative dispersion γ as a function of $\ln \tilde{N}^{(\infty)}$

as long as necessary. Actually the time for kinetics of this system is $t(G)$ with no connection with real time (certainly, the rate of nucleation has such connection). This phenomena is the reason for a smallness.

In dynamic conditions there is a time dependent parameter - the intensity of external source. So, there is no such a reason.

But here in the theory with averaged characteristics there is a property of a weak dependence of the total number of droplets on microscopic corrections for a free energy [3]. The same is valid also for fluctuation deviations. So there will be a weak effect of stochastic nucleation.

Because the reasons for smallness of effect in decay and dynamic conditions are different it is interesting to see whether they continue to act when the supersaturation is stabilized at some moment. Analytical results shows that the will be an overlapping of two reasons.

Really, if stabilization takes place at the period where the main consumers of vapor are going to appear then the majority of droplets appear in the
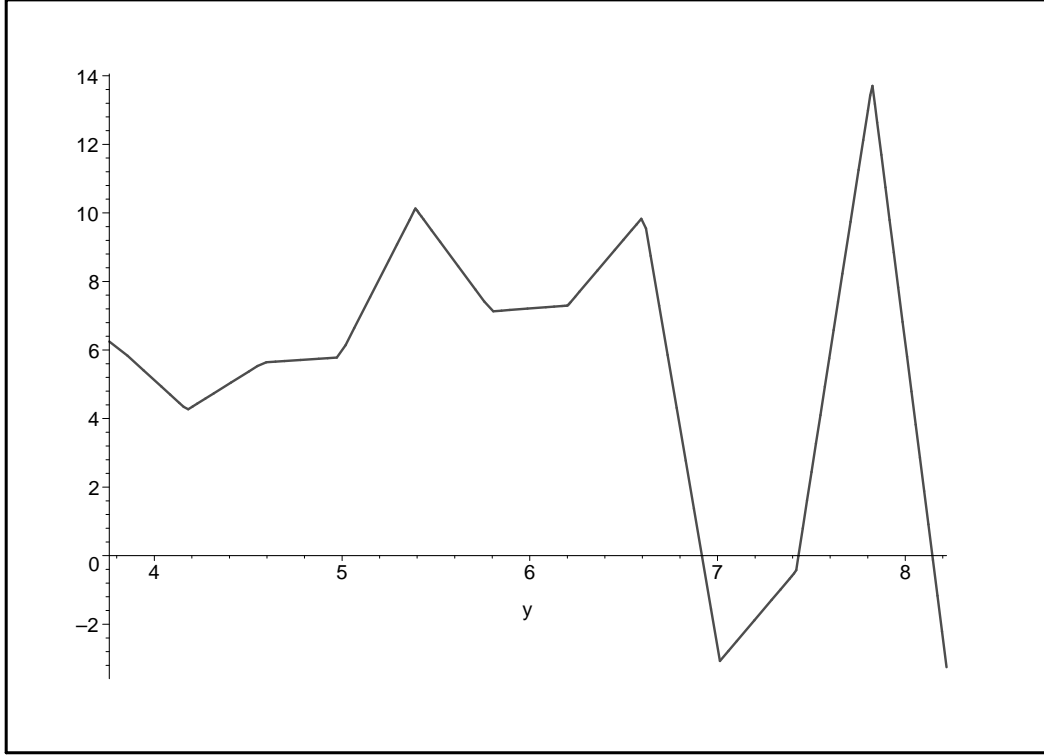
Figure 23: Shift in a droplets number as a function of $\ln \widetilde{N^{(\infty)}}$ for dynamic conditions

situation when there is no influence on the system. Then the situation for these droplets resembles decay conditions (and may be even better because the external supersaturation [12] is going to decrease). So the reason for the decay situation works here.

If stabilization takes place at the second cycle, then the behavior of supersaturation is governed by droplets formed in dynamic conditions and we have here the reason for smallness in dynamic conditions. In both situations the effect is small. Numerical results confirm this conclusion.

4.6 Conclusions

The main result of this publication is a correct definition of all main characteristics of stochastic nucleation. It is shown that the main role in stochastic effects belongs to all droplets, but not to the main consumers of vapor. Only
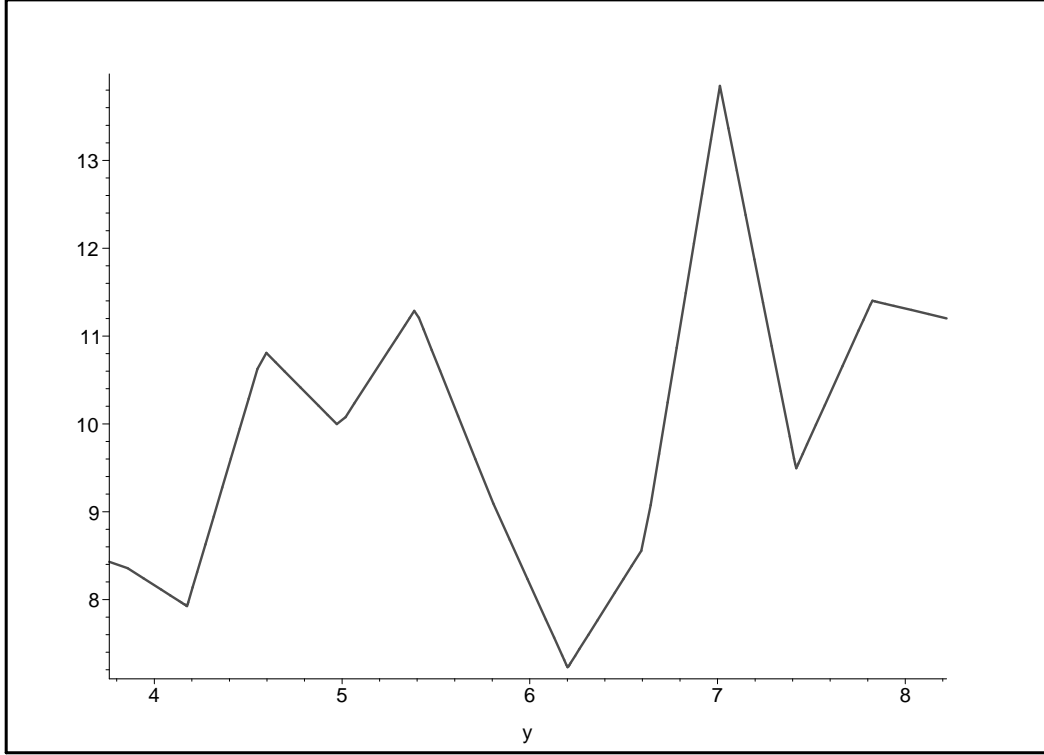
Figure 24:   Relative dispersion γ as a function of $\ln N^{\widetilde{(\infty)}}$ for dynamic conditions

the property of the nucleation conditions similarity allows us to solve the problem of account of all influences during the nucleation period.

When all disadvantages of [1], [10] are shown it is clear that these publications can not be considered as a solid base for nucleation investigation.

But why results obtained in [1], [10] are so close numerically to real values? The reason is that on a level of averaged characteristics there is a universality of nucleation process. So, the errors of [1], [10] cannot lead to a qualitatively wrong results.

One has to stress that all corrections obtained in this paper are also universal ones. Certainly, they are some coefficients in decompositions and the functional form of decomposition is prescribed now.

There is also a second specific reason for the smallness of an error in numerical values presented in [1]. The reason is the following

• The process of nucleation can be split in three sequential parts.

58

- The first part is the part where the main consumers of vapor were appeared. Here the vapor depletion is small

- The second (buffer) part is the part where conditions are ideal, the vapor depletion is small, but the droplets formed in this part can not attain big sizes even at the end of the whole nucleation period and, thus, can not consume enough vapor and they are not the main consumers of vapor

- The third part is the part where the depletion isn't small and droplets appeared in this part aren't the main consumers of vapor in the nucleation period.

- All parts have the lengths of one and the same scale.

Certainly this structure was not declared in [1] which made the derivation in [1] illegal.

The existence of the buffer part is necessary to balance the errors appeared from the fact that the fluctuations leads to to the absence of applicability of functional approximations for the nucleation kinetics. More correctly is to use the property of the "internal time of decay" which will be done separately.

It seems that all effects considered here are negligible. For simple systems it is really true. But for systems with more complex kinetic behavior these effects can be giant. One of such systems is already described theoretically and this description will be presented soon in a separate publication.

To compare results given here with the previous approach one can simply recall that the real error is the error in the relative deviation of dispersion from the standard value. In [1] this error is more than one quarter. Here the error is practically absent.

In diffusion regime of droplets growth one has to use another approach based on [4], [14]. In [14] an explicit description of nucleation with account of stochastic effects was constructed.

References

[1] Grinin A.P., F.M.Kuni, A.V. Karachencev, A.M.Sveshnikov Kolloidn. journ. (Russia) vol.62 N 1 (2000), p. 39-46 (in russian)

[2] Kurasov V.B. Manuscript published in VINITI 259495 from 19.09.95, 28 p. (in russian)

[3] Kurasov V.B. Phys.Rev.E vol. 49, p. 3948 (1994)

[4] Kurasov V.B., Physica A vol.226, p.117 (1996)

[5] Kurasov V. Preprint cond-mat@xxx.lanl.gov get 0410043

[6] Kurasov V. Preprint cond-mat@xx.lanl.gov get 0207024

[7] Wilson C.T.R. Condensation of water vapour in the presence of dust air and other gases. - Phil. Trans., 1898, v.189A, N11,p.265

Wilson C.T.R. On the condensation nuclei produced in gases by the action of Roentgen rays, uranium rays, ultraviolet rays and other agents. - Phil. trans., 1899, v.192A, N9, p.403

Wilson C.T.R. On the comparison efficiency as condensation nuclei of positively and negatively charged ions - Phil.Trans., 1900, v.193A, p.289

[8] Becker, R. and Doering, W., Ann.Phys. vol. 24, p.749 (1935)

Frenkel, J., Kinetic theory of liquids, Oxford University Press, New York, 1977

Lothe J., Pound G.M. J.Chem.Phys. vol.36, 2082 (1962)

[9] H.Reiss, J.Chem.Phys. 19, 482 (1951)

D.R.Warren and J.H.Seinfeld, Aerosol Science and Technology, 3, 135 (1984)

D.R.Warren and J.H.Seinfeld, Aerosol Science and Technology, 4, 31 (1985)

Clement C.F., Proceedings of the Royal Society, London A 398, 307 (1985)

D.R.Warren and J.H.Seinfeld, Journal of Colloid and Interface Science, 105, 136 (1985)

Barrett J.C., Journal Aerosol Science, 31, 51 (2000)

Barrett J.C., Baldwin T.J., Journal Aerosol Science, 31, 633 (2000)

[10] Grinin A.P., A.V. Karachencev, Ae. A. Iafiasov Vestnik Sankt-Peterburgskogo universiteta (Scientific journal of St.Petersburg university) Series 4, 1998, issue 4 (N 25) p.13-18 (in russian)

[11] Grinin A.P., Kuni F.M., Sveshnikov A.M. Koll. Journ., 2001, volume 63, N6, p.747-754

[12] Kurasov V.B. Universality in kinetics of the first order phase transitions. Chemistry research Institute of St.Petersburg State University. St.Petersburg, 1997, 400 p.

[13] Kurasov V.B. Development of the universality conception in the first order phase transitions. Chemistry research Institute of St.Petersburg State University. St.Petersburg, 1998, 125 p.

[14] Kurasov V.B. Heterogeneous condensation in dense media, Phys.Rev.E Vol 63, 056123, (2001)

[15] Kuni F.M., Grinin A.P., Kurasov V.B., Heterogeneous nucleation in vapor flow, In: Mechanics of unhomogenenous systems, Ed. by G.Gadiyak, Novosibirsk, 1985, p. 86 (in Russian)